A TREATISE ON CHEMISTRY

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A
TREATISE ON CHEMISTRY

BY

THE RIGHT HONOURABLE SIR H. E. ROSCOE, F.R.S.

AND

C. SCHORLEMMER, F.R.S.

VOLUME II
THE METALS
PART II

> "*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723.

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B. MOUAT JONES AND OTHERS

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THE FOLLOWING ARE THE CHIEF CONTRACTIONS EMPLOYED IN THIS VOLUME

Abbreviated Title	Journal
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Mines	Annales des Mines.
Arch. Néerland.	Archives Néerlandaises des Sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Biochem. Zeit.	Biochemische Zeitschrift.
Brit. Assoc. Reports	Reports of the British Association.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Soc. chim.	Bulletin de la Société chimique de Paris.
Chem. Centr.	Chemisches Centralblatt.
Chem. News	Chemical News.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Gazz.	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Pharm.	Journal de Pharmacie.
J. Physical Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Journ. Chem. Soc.	Journal of the Chemical Society.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Mem. Manch. Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Min. Mag.	Mineralogical Magazine.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Phil. Mag.	Philosophical Magazine.

CONTRACTIONS EMPLOYED IN THIS VOLUME

ABBREVIATED TITLE	JOURNAL
Phil. Trans.	Philosophical Transactions of the Royal Society.
Pogg. Ann.	Poggendorff's Annalen der Physik und der Chemie.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English Version).
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Sitzungsber. K. Akad. Wiss. Berlin	Sitzungsberichte der königlich preussischen Akademie der Wissenschaften zu Berlin.
Zeit. anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. Chem.	Zeitschrift für Chemie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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CHEMISTRY

THE METALS (*continued*)

GROUP IV.

Sub-group (*a*)	*Sub-group* (*b*)
Carbon.	Silicon.
Titanium.	Germanium.
Zirconium.	Tin.
(Cerium).	Lead.
Hafnium.	
Thorium.	

374 In this group there is no well-defined division of the elements composing it into two distinct sub-groups, such as is noticeable in the others of the first seven groups, and the differences observable between the members of the odd and even series are only of minor importance.

Cerium probably belongs to this group, but as its chemistry is so intimately connected with that of the other members of the group of rare earth metals it has been described among them.

The first two members of this group, carbon and silicon, have already been described among the non-metallic elements. Both exist in the amorphous and crystalline states, silicon melting only at a very high temperature, whilst carbon has not yet been melted, although it volatilises at the highest attainable temperatures. The remaining elements all have metallic properties, and, with the exception of tin and lead, possess high melting points; in the compact state they undergo at most a surface oxidation in the air at the ordinary temperature, but when strongly heated readily combine with oxygen, and, except in the case of lead, the oxide formed in presence of an excess of oxygen is the *dioxide*. The dioxides of the members having the lower atomic weights, including those of carbon and silicon, behave chiefly as acid-forming oxides, but they become more basic as the atomic weight of the element increases. These oxides correspond in each case with a series of salts in which the element is tetravalent, and, except in the case of lead, this series includes the most important compounds. Lead in its most characteristic compounds is divalent, and, as is so frequently the case with elements having a high atomic weight, it presents many resemblances to the elements having the next lowest and next highest atomic weights, viz., thallium and bismuth.

A very characteristic series of double salts with the alkali halides is yielded by the tetrahalogen derivatives of most of these elements, the double fluorides, which have the general formula $M^I_2M^{IV}F_6$, being the most important. In the case of silicon, titanium, germanium, zirconium, and tin, these compounds are isomorphous, but this appears not to be the case with the thorium compound. The corresponding salt of lead has not been prepared, but an acid salt, $PbF_4,3KF,HF$, exists, which is isomorphous with the analogous tin salt, $SnF_4,3KF,HF$.

Carbon is distinguished from all other elements by the property possessed by its atoms of uniting together in open or closed chains, forming nuclei, which may contain as many as sixty atoms, and which, in combination with the other elements, give rise to the immense number of carbon compounds. The same property is observable to a much smaller extent in silicon, but not in the other members of the group. In addition to the typical elements, carbon and silicon, only germanium, tin, and lead, *i.e.*, the members of the "odd" series, yield organometallic derivatives.

THE TITANIUM GROUP.

TITANIUM. Ti = 48·1. At. No. 22.

375 The Rev. William Gregor[1] in 1789 discovered a new metal contained in the mineral menachanite or ilmenite, occurring in Cornwall. In 1795 Klaproth investigated the composition of the mineral rutile, and discovered in it a new metal to which he gave the name of titanium. In a subsequent investigation of ilmenite, in 1797, he found that the metal which that mineral contained was titanium. Klaproth found that rutile consisted mainly of titanium dioxide, but he did not succeed in obtaining the oxide in the pure state, this having been first accomplished by Rose in 1821.

Titanium, though not an abundant element, is very widely distributed. It is not found in the metallic state, but occurs as the dioxide, TiO_2, in three minerals, rutile, brookite, and anatase, which possess different crystalline forms; in combination with ferrous and ferric oxides in titanic iron ore or ilmenite, $FeTiO_3$; and with lime and oxide of iron in perofskite, $(Ca,Fe)TiO_3$, as well as in titanite or sphene, $CaTiSiO_5$, schorlomite, $Ca(Ti,Fe)SiO_5$, and keilhauite, $CaYt(Ti,Al,Fe)SiO_5$. Magnetic iron ore also frequently contains larger or smaller quantities of titanium which finds its way into many blast-furnace slags and pig-irons. Titanium occurs in small quantity in several other minerals, and traces have been found in trap and basalt, in many amphiboles and micas, and in garnet; hence it occurs in most fertile soils in quantities between 0·3 and 0·6 per cent.,[1] in many clays, and likewise in certain mineral waters. It has been found in human and ox flesh and bone,[2] and occurs in the ashes of all plants[3] in quantities up to 0·27 per cent.,[4] and in many peats.[5] Its presence has been detected in certain meteorites, and it forms an important constituent of the solar atmosphere.

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[1] *Crell. Ann.*, 1791.

Preparation of Metallic Titanium.—Metallic titanium is difficult to obtain in the pure condition; the usual methods for the reduction of the oxide, such as heating with metallic sodium and magnesium, yield products which still contain considerable quantities of titanium monoxide, and the product obtained by the action of sodium on halogen derivatives of titanium also usually contains small quantities of the monoxide, formed by the action of the moisture present, and of the nitride, obtained by the direct union of the metal with nitrogen, which it is almost impossible completely to exclude. Owing to the extreme readiness with which titanium and nitrogen combine at high temperatures, and to the metallic appearance of the nitride, this compound was mistaken by the earlier investigators for the metal itself, as was also the compound which it forms with carbon and nitrogen, now known as titanium cyanonitride.

Moissan fused carbon with an excess of titanium dioxide at a very high temperature in the electric furnace. Three distinct layers were found in the solidified product, the uppermost consisting of titanium containing about 5 per cent. of carbon, the second of the nitride, and the third of titanium monoxide.

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[1] Geilmann, *J. Landw.*, 1920, **68**, 107.

[2] Baskerville, *J. Amer. Chem. Soc.*, 1899, **21**, 1099.

[3] Wait, *J. Amer. Chem. Soc.*, 1896, **18**, 402; Lippmann, *Ber.*, 1897, **30**, 3037.

[4] Geilmann, *J. Landw.*, 1920, **68**, 107.

[5] Baskerville, *J. Amer. Chem. Soc.*, 1899, **21**, 402.

The top layer was heated again with an excess of titanium dioxide; the quantity of carbon was reduced to 2 per cent., and the product was free from nitrogen and silicon.[1]

Nilson and Pettersson,[2] by acting on titanium tetrachloride with sodium in an air-tight cylinder of mild steel at a red heat prepared metallic titanium in yellow scales, which had frequently a bluish surface colour. These, however, still contained a considerable quantity of oxygen, probably as the monoxide. A still less pure product is obtained by heating potassium titanofluoride with sodium. A very much purer product has been obtained by heating titanium oxide in an evacuated iron vessel with calcium shavings.[3]

Metallic titanium has been prepared by Stähler and Bachran[4] by heating the dichloride in a current of hydrogen to 1100°, when the reaction: $2TiCl_2 = TiCl_4 + Ti$ takes place. A method of preparing titanium of 99·7 per cent. purity has been described by Podszus.[5] The method consists in placing a mixture of sodium and titanium tetrachloride in a steel bomb filled with hydrogen or carbon dioxide and containing a number of polished steel balls. The bomb is closed by a powerful screw and sealed with molten lead. The bomb being closed, the whole is rotated at 200° for 20–40 hours to produce an intimate mixture. The reaction is started by heating the bomb strongly for a few minutes. When the reaction is complete the bomb is cooled from the top downwards. The product is titanium in the form of minute crystals which are highly reactive.

Titanium is a brittle, grey metal, which is hard enough to scratch steel and quartz. It has a density 4·87 and melts at 1795°. It is stable in the air at the ordinary temperature, but burns brilliantly in oxygen at 610°. Titanium combines with nitrogen with extreme readiness, in this respect resembling boron and magnesium; the reaction commences at about 800°, and the nitride is also formed together with the oxide when the metal burns in the air.

Titanium combines with the halogens when heated to form the tetrahalides; with chlorine the action takes place at 350°, with bromine at 360° and with iodine at 400°. It dissolves slowly in dilute sulphuric acid and in concentrated hydrochloric acid, with liberation of hydrogen and formation of violet salts. It is converted into titanic acid by nitric acid and aqua regia and decomposes steam at 700–800°. Moissan[1] has distilled the metal in the electric furnace by the use of a current of great intensity, the metal condensing in small crystals.

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[1] Moissan, *Compt. rend.*, 1895, **120**, 290.

[2] *Zeit. physikal. Chem.*, 1887, **1**, 25.

[3] Wedekind, *Annalen*, 1913, **395**, 149.

[4] *Ber.*, 1911, **44**, 2907.

[5] *Zeit. anorg. Chem.*, 1917, **99**, 123.

Metallic titanium in the form of its alloys is used in the steel industry. Steel to which a small quantity of titanium has been added is improved in tensile strength and is largely used on the American railways and for bridge construction.

TITANIUM COMPOUNDS.

TITANIUM AND OXYGEN.

376 Titanium combines with oxygen to form a number of oxides, the most important being:

Titanium monoxide, TiO.
Titanium sesquioxide, Ti_2O_3.
Titanium dioxide, TiO_2.
Titanium peroxide, TiO_3.

Titanium Monoxide, TiO, is obtained in the form of black, prismatic crystals by heating the dioxide strongly in the electric furnace,[2] and is also formed, together with magnesium titanate, when titanium dioxide is heated with the requisite quantity of magnesium powder:[3]

$$2TiO_2 + Mg = TiO + MgTiO_3.$$

The hydroxide, $Ti(OH)_2$, is formed as a black precipitate when an alkali hydroxide is added to a solution of titanium dichloride. It is readily oxidised in air to hydrated titanium dioxide.

Titanium Sesquioxide, Ti_2O_3, is obtained by strongly igniting titanium dioxide in a current of hydrogen and allowing the product to cool in the gas. The same oxide may also be obtained as a copper-coloured, lustrous, crystalline mass, together with the trichloride and oxychloride of titanium, by passing a mixture of hydrogen and the vapour of titanium tetrachloride over white-hot titanium dioxide. It is not attacked by nitric or hydrochloric acids, but sulphuric acid dissolves it with formation of a violet solution (Ebelmen).

The *hydrated sesquioxide* is formed by digesting a solution of titanic acid in hydrochloric acid with metallic copper at 20–40°; the solution attains a violet-blue colour, and when poured into aqueous ammonia yields a dark brown precipitate of titanous hydroxide (Fuchs). The hydroxide is formed also when a solution of the trichloride is precipitated by alkalis.

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[1] *Compt. rend.*, 1906, 142, 673.
[2] Moissan, *Compt. rend.*, 1892, 115, 1034.
[3] Winkler, *Ber.*, 1890, 23, 2658.

When titanium sesquioxide is shaken with milk of lime in the presence of oxygen it is oxidised to the dioxide. More oxygen is absorbed than is necessary for this change, whilst hydrogen peroxide is formed in amount corresponding to the whole of the oxygen absorbed. Water must therefore take part in the reaction, and the phenomenon is probably a case of autoxidation (see Vol. I., p. 253). In the same way, when the sesquioxide is oxidised by a solution of chromic acid in the presence of potassium iodide, or by potassium permanganate in the presence of tartaric acid, titanic acid is formed and at the same time oxidation of the potassium iodide or tartaric acid is brought about.[1]

Titanium Dioxide, TiO_2, is trimorphous, occurring as three different minerals, rutile, anatase, and brookite. Rutile crystallises in tetragonal prisms, having a specific gravity of 4·18–4·25, isomorphous with those of tin dioxide or cassiterite, and possessing an adamantine lustre and a brown or reddish colour. Anatase crystallises in a totally different form of the tetragonal system, has a specific gravity of 3·82–3·95, and a brown or black colour. Brookite crystallises in flat, rhombic prisms and has a specific gravity of 4·12–4·23.

Amorphous titanium dioxide is obtained by the decomposition of aqueous titanium chloride by ammonia, the precipitate being washed, dried, and ignited; or it may be directly prepared from rutile or titanic iron ore. In order to prepare the pure oxide from rutile, the finely-powdered mineral is fused with three times its weight of potassium carbonate, the solidified mass powdered and dissolved, in a platinum vessel, in dilute hydrofluoric acid, potassium titanofluoride being thus formed and the ferric oxide left free from titanium. The mass is then heated with sufficient water to dissolve the whole of the titanium double salt, the liquid boiled, and filtered hot. On cooling, the mass of the titanofluoride crystallises out, and this, after washing with cold water, may be purified by recrystallisation. The titanofluoride is then dissolved in hot water and the titanium precipitated by ammonia as titanic hydroxide containing ammonia, which on ignition yields pure titanium dioxide (Wöhler). Pure titanic oxide may also be obtained from titanic ore in a similar manner, or by fusing it with potassium bisulphate, or by igniting it in a mixture of chlorine and hydrochloric acid, when ferric chloride is volatilised (Friedel and Guérin):

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[1] Manchot and Richter, *Ber.*, 1906, 39, 320, 488.

$$2FeTiO_3 + 4HCl + Cl_2 = 2FeCl_3 + 2TiO_2 + 2H_2O.$$

Amorphous titanium dioxide is a white, tasteless powder which when gently heated has a lemon-yellow colour, and when strongly ignited appears brown. It has a specific gravity of from 3·89 to 3·95, and when very strongly heated this rises to 4·25.

When it is heated with microcosmic salt (Ebelmen) or with borax (G. Rose) for some time to a white heat, fine crystals of rutile are obtained, which have a specific gravity of 4·26. Crystalline titanium dioxide can also be obtained by passing the gases obtained by decomposing molten potassium titanofluoride with hydrogen chloride through a hot platinum tube into which a current of moist air and hydrogen is also passed. In this way Hautefeuille[1] has shown that by treatment at a temperature not exceeding the boiling point of cadmium (778°), anatase is produced, the crystals of which have a specific gravity of 3·7 to 3·9; at a temperature of about 1,000°, steel-blue coloured rhombic crystals of brookite are obtained, which have a specific gravity of 4·1, and closely resemble the natural crystals from Miask. At still higher temperatures again, rutile is produced, so that this last is the only form which is stable at a high temperature, and in an acid or moist atmosphere.[2]

At the temperature of the oxy-hydrogen flame titanium dioxide fuses, forming a thin liquid, which solidifies to a confused crystalline mass.

In its chemical properties titanium dioxide closely resembles the corresponding silicon dioxide, behaving as an acid anhydride. It is insoluble in water, hydrochloric acid, and dilute sulphuric acid, although it dissolves when digested for some time with hot concentrated sulphuric acid. The amorphous oxide dissolves on fusion with alkalis or alkali carbonates, unless it has been strongly ignited, forming the titanates, and also dissolves slowly in fused potassium hydrogen sulphate, yielding a clear mass which dissolves perfectly in warm water. When this solution is boiled, the hydrated dioxide is precipitated. Titanium dioxide corresponds to the most important series of titanium salts in which the metal is tetravalent.

Titanic Acid and the Titanates.—As is the case with the analogous silicic acid, several hydrates of varying composition are known. There appears to be little doubt that the hydrates *orthotitanic acid*, $Ti(OH)_4$, and *metatitanic acid*, $TiO(OH)_2$, exist, but in addition others have been prepared containing quantities of water intermediate between the amounts required for these two formulæ, and also with less than that required by the latter formula. These may possibly be the hydrates corresponding to the complex titanic acids, but they have not been obtained of sufficiently definite composition to enable this to be ascertained.

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[1] *Ann. Chim. Phys.*, 1865, [4], 4. 129.

[2] Friedel and Guérin, *Bull. Soc. chim.*, 1874, 22. 482.

Orthotitanic Acid, $Ti(OH)_4$, is obtained by adding an alkali to a cold hydrochloric acid solution of a titanate, and forms a voluminous white precipitate which is soluble in dilute hydrochloric acid and sulphuric acid, and loses water on drying, forming other hydrates. When heated it is converted into the anhydride, the reaction being accompanied by evolution of light. When allowed to remain under water it is gradually converted into metatitanic acid.[1]

Metatitanic Acid, $TiO(OH)_2$, is obtained by boiling a solution of orthotitanic acid in hydrochloric acid, or by the action of nitric acid of specific gravity 1·25 on titanium. It is insoluble in acids except concentrated sulphuric acid. When heated it is converted into the anhydride without emission of light.

The other hydrates also are frequently spoken of as "ortho" or "meta" acids, according as they are soluble or insoluble in dilute acids.

By the dialysis of a hydrochloric acid solution of orthotitanic acid, Graham obtained a solution of colloidal titanic acid, and von der Pfordten has also obtained the acid as a colourless jelly.[2]

Potassium Titanate, K_2TiO_3, is formed as a yellow, fibrous mass when the dioxide is fused with potassium carbonate. On boiling titanic acid with caustic potash and evaporating the solution, colourless, readily soluble prisms of $K_2TiO_3,4H_2O$ are deposited. When a hydrochloric acid solution of titanic acid is precipitated with potassium carbonate, an amorphous precipitate of potassium trititanate, $K_2Ti_3O_7,2H_2O$, is thrown down, and this in presence of hydrochloric acid is converted into a hexatitanate, $K_2Ti_6O_{13},2H_2O$. The fused anhydrous normal salt, when treated with water in excess, also yields a trititanate, $K_2Ti_3O_7,3H_2O$, as a fine crystalline powder.

When sodium carbonate and titanium dioxide are fused the

[1] Wagner, *Ber.*, 1888, 21, 960.

[2] *Annalen*, 1887, 237, 213.

three *sodium titanates*,[1] $Na_8Ti_5O_{14}$, $Na_2Ti_3O_7$, and Na_2TiO_3, are obtained; of these, $Na_8Ti_5O_{14}$ crystallises in forms resembling augite and has a refractive index greater than 1·74.

Calcium Titanate, $CaTiO_3$.—This occurs in the Urals, in the valley of Zermatt in Switzerland, and at Magnet Cove, Arkansas, as the mineral perofskite, which contains in addition 1 to 6 per cent. of ferrous oxide, as well as traces of manganese and magnesium. It forms rhombic crystals having a metallic or adamantine lustre, a yellow or iron-black colour, and a specific gravity of 4·0. The crystals can be artificially obtained by fusing a mixture of potassium carbonate and titanium dioxide with a large excess of calcium carbonate.[2]

Calcium Titanosilicate, $CaTiSiO_5$, is found as titanite or sphene in brown, green, or black monoclinic crystals, having an adamantine or resinous lustre and a specific gravity of 3·4 to 3·56, occurring imbedded in granite, gneiss, mica-schist, and granular limestone. Titanite can be obtained artificially by fusing calcium chloride with titanium dioxide and silica. The mineral guarinite has the same composition as titanite, and is found in tetragonal crystals, having a specific gravity of 3·487, in small cavities in a greyish trachyte at Monte Somma.

Ilmenite, or Titanic Iron Ore, $FeTiO_3$.—This mineral, the one in which titanium was first discovered, occurs tolerably widely distributed, and crystallises in black, hexagonal crystals. One of its most important localities is Krageroe, in Norway. Fine crystals are also found in Warwick Co., New York, and vast deposits occur at Bay St. Paul, in Canada. It is frequently found in the finely-divided state as sand on the shores of the Mersey opposite Liverpool, in New Zealand, and elsewhere. Its specific gravity ranges from 4·5 to 5, and its composition is a variable one. It was thought to be an isomorphous mixture of the sesquioxides of titanium and iron, but is now regarded as a derivative of titanium dioxide. Many ilmenites contain magnesia,[3] and the formula has sometimes been written as $(Fe,Mg)O,TiO_2$.

Geikielite, a rare mineral from Ceylon, is a ferro-magnesian titanate containing a high proportion of magnesia.[4]

Titanium Trioxide, or *Titanium Peroxide*, TiO_3, is obtained by dropping titanium chloride into dilute alcohol and adding a arge excess of hydrogen peroxide to the solution. Ammonia, mmonium carbonate, or potash is then added, and after a time bright yellow precipitate separates out. The precipitate con-sts of a hydrate of titanium trioxide, $TiO_3,3H_2O$, which retains ater and salts very persistently, and dissolves in hydrochloric id with evolution of a little chlorine and formation of a yellowish-red solution.[1]

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[1] Niggli, *Zeit. anorg. Chem.*, 1916, 98, 241.

[2] *Ibid.*

[3] Penfield and Foote, *Amer. J. Sci.*, 1897, [4], 4, 108.

[4] Crook and Jones, *Mineralogical Magazine*, 1906, 14, 160.

When titanium trioxide is treated at 0° with hydrogen peroxide and potash and alcohol are then added, crystals of *potassium peroxide hypertitanate*, $K_2O_4,TiO_3,K_2O_2,10H_2O$, separate out, whilst if soda is used in place of potash the compound formed has the composition $(Na_2O_2)_4,Ti_2O_7,10H_2O$. These substances are stable at 0°, but lose oxygen at ordinary temperatures.[2]

TITANIUM AND THE HALOGENS.

377 *Titanium Trifluoride*, TiF_3, is obtained as an insoluble violet powder by igniting potassium titanofluoride in a current of hydrogen and treating the product with hot water. It is also formed when the potassium titanofluoride is reduced in aqueous solution by zinc and hydrochloric acid or sodium amalgam. It combines with ammonium fluoride, forming the double salts $(NH_4)_2TiF_5$ and $(NH_4)_3TiF_6$.

Titanium Tetrafluoride, TiF_4, is obtained by the action of fluorine on warm, finely-powdered titanium, or of anhydrous hydrofluoric acid on titanium tetrachloride at 100–120°, or on powdered titanium at a red heat,[3] and also by the action of liquid anhydrous hydrofluoric acid on the tetrachloride.[4] It may also be prepared by heating barium titanofluoride to a red heat.[5] It is a white solid at the ordinary temperature, boils at 284°, and has the specific gravity 2·798 at 27·5°, whilst its vapour density at 444° corresponds with the formula TiF_4. It is very hygroscopic and dissolves in water to a clear solution, which on evaporation deposits crystals of $TiF_4,2H_2O$. With dry ammonia it forms the compound $TiF_4,2NH_3$, which sublimes without decomposition and is soluble in water. Titanium tetrafluoride is decomposed by hot sulphuric acid with formation of the dioxide.

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[1] Classen, *Ber.*, 1888, 21, 370.

[2] Melikoff and Pissarjewsky, *Ber.*, 1898, 31, 678.

[3] Ruff and Ipsen, *Ber.*, 1903, 36, 1777.

[4] Ruff and Plato, *Ber.*, 1904, 37, 673.

[5] Emich, *Monatsh.*, 1904, 25, 1907.

When titanium dioxide is dissolved in hydrofluoric acid a syrupy liquid is obtained, which probably contains *hydrogen titanofluoride*, H_2TiF_6. The *titanofluorides* are isomorphous with the silicofluorides, zirconofluorides, and stannifluorides.

Potassium Titanofluoride or *Potassium Fluotitanate*, K_2TiF_6.—This salt may be prepared by the action of potassium hydrogen fluoride on a solution of titanium dioxide in excess of concentrated hydrofluoric acid. It crystallises in small, lustrous leaflets, which may be recrystallised without change from hydrofluoric acid.[1] The hydrated salt, K_2TiF_6,H_2O, is prepared either by adding potash to aqueous hydrogen titanofluoride (Berzelius), or, according to Wöhler, by fusing titanium dioxide in a platinum crucible with twice its weight of potassium carbonate and dissolving the fused and pulverised mass in a platinum dish in the requisite quantity of dilute hydrofluoric acid. The potassium salt then crystallises out in shining scales closely resembling those of boric acid and belonging to the monoclinic system (Marignac); they may be dried between filter paper and recrystallised from boiling water. It loses its water at 100° and melts without decomposition at a white heat. The anhydrous salt may be obtained from the hydrated salt by recrystallisation from concentrated hydrofluoric acid (Marchetti). When a warm solution of potassium titanofluoride is treated with hydrogen peroxide, *potassium titanoperoxyfluoride*, $TiO_2F_2,2KF$, is formed.[2]

Sodium Titanofluoride, Na_2TiF_6, is obtained in a similar manner to the preceding salt in hexagonal prisms most probably isomorphous with sodium silicofluoride (Marignac). A solution containing an excess of hydrofluoric acid deposits small, glistening, rhombic crystals having the composition $Na_2TiF_6,NaHF_2$.

Ammonium Titanofluoride, $(NH_4)_2TiF_6$.—This salt was obtained by Berzelius, in rhombohedra isomorphous with the corresponding tin compound, by neutralising hydrogen titanofluoride with ammonia. Another salt of composition

$$(NH_4)_2TiF_6,NH_4F$$

separates in tetragonal crystals from a solution of the preceding salt in an excess of ammonium fluoride.

Titanium Dichloride, $TiCl_2$, was obtained by Friedel and Guérin[3] by passing dry hydrogen at a dull red heat over titanium trichloride. This compound is a very hygroscopic light brown powder, which can be volatilised in hydrogen at a red heat withou fusion. It burns like tinder on exposure to air, giving off fumes of titanium tetrachloride and leaving a residue of titanium dioxide. It hisses when thrown into water, evolving hydrogen and yielding a yellow liquid.

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[1] Marchetti, *Zeit. anorg. Chem.*, 1895, **10**, 66.

[2] Piccini, *Zeit. anorg. Chem.*, 1895, **10**, 438.

[3] *Ann. Chim. Phys.*, 1876, [5], 7, 24. Stähler and Bachran, *Ber.*, 1911, **44**, 2906.

Titanium Trichloride, $TiCl_3$.—When the vapour of titanium tetrachloride mixed with hydrogen is passed through a red-hot tube, dark violet scales of the trichloride are deposited (Ebelmen). It may also be obtained by heating titanium tetrachloride in a closed tube with molecular silver at 180–200°:

$$TiCl_4 + Ag = TiCl_3 + AgCl.$$

If the mixture thus obtained is heated more strongly, the reverse action takes place (Friedel and Guérin). Titanium trichloride has also been obtained by the electrolytic reduction of a solution of titanium tetrachloride in dilute hydrochloric acid, violet crystals of the composition $TiCl_3,6H_2O$ being deposited when the resulting liquid is either evaporated *in vacuo* or saturated at 0° with dry hydrochloric acid.[1]

Titanium trichloride is non-volatile, and on heating decomposes into the dichloride and tetrachloride. When heated in the air, thick vapours of titanium tetrachloride are emitted and titanium dioxide is left behind. It readily deliquesces on exposure to moist air and dissolves in water with evolution of heat, yielding a reddish-violet solution.

Titanium trichloride is a powerful reducing agent. Thus when boiled with aqueous sulphurous acid, sulphur separates out, whilst nitric acid and the nitrates are reduced by it to ammonia (Knecht), and the salts of gold, silver, and mercury to the metals. Standard solutions of titanium trichloride have been used in volumetric analysis for the estimation of ferric iron and also for the analysis of a number of colouring matters.[2]

Double compounds of titanium trichloride with the chlorides of rubidium and cæsium have been prepared,[3] having the compositions $TiCl_3,2RbCl,H_2O$ and $TiCl_3,2CsCl,H_2O$.

Titanium Tetrachloride, $TiCl_4$.—Metallic titanium does not combine with chlorine at the ordinary temperature, but when heated to 350° it burns in the gas with brilliancy, forming the tetrachloride (Wöhler). According to Friedel and Guérin, titanium dioxide is converted in presence of chlorine at a white heat into titanium tetrachloride, oxygen being evolved. The tetrachloride is readily obtained by passing dry chlorine over a heated mixture of titanium dioxide and carbon, whilst it is also formed, together with carbonic oxide and hydrogen chloride, when chloroform or carbon tetrachloride vapour is passed over heated titanium dioxide.[1]

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[1] Polidori, *Zeit. anorg Chem.*, 1899, **19**, 300; Stähler, *Ber.*, 1904, **37**, 4405; Spence and Son, German Patent, 154542.

[2] Knecht, *Ber.*, 1903, **36**, 166; Knecht and Hibbert, *ibid.*, 1903, **36**, 1549; 1905, **38**, 3318; 1907, **40**, 3819; 1910, **43**, 3455.

[3] Stähler, *Ber.*, 1904, **37**, 4405.

It may also be obtained by heating powdered ferrotitanium in a current of chlorine or by treating ferrotitanium with hydrochloric acid to dissolve out most of the iron, and heating the dried residue of titanic oxide with carbon in a stream of chlorine.[2] It is a mobile, transparent, colourless liquid, having a specific gravity of 1·7604 at 0° (Pierre). It freezes[3] at −23°, and boils at 136·4° (134·8°, Emich), its vapour having the normal specific gravity of 6·836 (Dumas). It possesses a penetrating acid odour, and emits dense white fumes on exposure to air.

Titanium tetrachloride is decomposed by an excess of water with formation of titanic acid, which remains dissolved in the aqueous hydrochloric acid simultaneously formed. By careful addition of water it is possible to replace the chlorine atoms one by one by hydroxyl, yielding the compounds $TiCl_3(OH)$, $TiCl_2(OH)_2$, and $TiCl(OH)_3$, whilst an excess of water converts it into $Ti(OH)_4$.

Titanium tetrachloride yields a large number of crystalline compounds with other chlorides analogous to those formed by stannic chloride.[4] When dry ammonia gas is passed over titanium tetrachloride it is rapidly absorbed, and a very hygroscopic powder, $TiCl_4,4NH_3$, is formed which when ignited yields a yellow sublimate of $TiCl_4,3NH_4Cl$. Other compounds with ammonia[5] have been prepared of the formulæ $TiCl_4,6NH_3$ and $TiCl_4,8NH_3$; these are solid bodies which lose ammonia readily in air and on extracting with liquid ammonia yield ammonium chloride and a dark yellow substance, *titanamide*, $Ti(NH_2)_4$.

Titanium tetrachloride dissolves in concentrated hydrochloric acid to form a yellow solution containing *chloro-titanic acid*,

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[1] Renz, *Ber.*, 1906, **39**, 249.

[2] Vigouroux and Arrivant, *Bull. Soc. chim.*, 1907, [4], **1**, 19.

[3] Emich, *Monatsh.*, 1904, **25**, 907.

[4] See Rosenheim, and Schütte, *Zeit. anorg. Chem.*, 1901, **26**, 239; Ruff and Ipsen, *Ber.*, 1903, **36**, 1777.

[5] Stähler, *Ber.*, 1905, **38**, 2619. See also Rosenheim and Schütte, *Zeit. anorg. Chem.*, 1901, **26**, 239.

H_2TiCl_6,[1] and when this solution is treated with the theoretica quantity of ammonium chloride yellow crystals of ammonium chlorotitanate separate.

Titanium Oxychloride, $Ti_2O_2Cl_4$, is obtained, together with the trichloride, when a mixture of hydrogen and the vapour of titanium tetrachloride is passed over the ignited dioxide. It forms reddish-brown, translucent crystals, which burn when heated in the air with formation of the dioxide and the tetrachloride (Friedel and Guérin). Other oxychlorides also have been prepared

Titanium Tribromide, $TiBr_3,6H_2O$, is obtained in unstable, deliquescent, violet-coloured crystals when a solution of titanium tetrabromide in hydrobromic acid is electrolysed, and the liquid then saturated with hydrobromic acid gas.[2]

Titanium Tetrabromide, $TiBr_4$, is obtained when hydrobromic acid is passed over the heated chloride[3] as an amber-yellow, hygroscopic, finely crystalline mass which has a specific gravity of 2·6, melts at 39°, and boils at 230°.[4]

It is readily hydrolysed by water, forming oxybromides, $TiBr_2OH$ and $2TiBr(OH)_3,2H_2O$. It combines directly with ammonia, forming the compound $TiBr_4,8NH_3$. It dissolves in hydrobromic acid to form a blood-red solution which contains *bromotitanic acid*, H_2TiBr_6. When treated with ammonium chloride, the ammonium salt of this acid, $(NH_4)_2TiBr_6,2H_2O$, separates in dark red crystals.

Titanium Di-iodide, TiI_2,[5] is prepared by heating the tetra-iodide in a current of hydrogen and mercury vapour. It is a black compound which forms non-volatile, hygroscopic leaflets of density 4·3. It is decomposed by water and is soluble in boiling hydrochloric acid to form a blue solution.

Titanium Tri-iodide, $TiI_3,6H_2O$.—Deliquescent, violet crystals of this composition are formed by the electrolytic reduction of a solution of the tetra-iodide in hydriodic acid.[6]

Titanium Tetra-iodide, TiI_4, is produced when iodine vapour is passed over heated titanium (Weber); also when dry hydriodic acid is passed into titanium tetrachloride, which is gradually heated up to its boiling point. The small quantity of free iodine giving a violet tinge may be removed by three or four distillations in a stream of hydrogen (Hautefeuille). A third process consists in passing the vapour of titanium tetrachloride mixed with hydrogen and iodine vapour through a tube heated to redness. Titanium tetra-iodide forms a brittle mass having a reddish-brown colour and metallic lustre. It melts at 150° to a yellowish-brown liquid, which solidifies on cooling in fine octahedral crystals. It distils without decomposition at a temperature slightly above 360°, giving rise to orange-coloured vapours. The specific gravity of its vapour at 440° has the normal value of 18·054. It fumes strongly in the air and dissolves readily in water.

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[1] Kowalewsky, *Zeit. anorg. Chem.*, 1900, **25**, 189. Rosenheim and Schütte, *Zeit. anorg. Chem.*, 1901, **26**, 239.

[2] Stähler, *Ber.*, 1904, **37**, 4405.

[3] Thorpe, *Journ. Chem. Soc.*, 1885, **47**, 126.

[4] Duppa, *Proc. Roy. Soc.*, 1857, **8**, 42.

[5] Defacqz and Copaux, *Bull. Soc. chim.*, 1908, [3], 898.

[6] Stähler, *Ber.*, 1904, **37**, 4405.

TITANIUM AND SULPHUR.

378 Titanium combines with sulphur to form the sulphides, TiS_2, Ti_2S_3, and TiS, corresponding to the oxides of the metal.

Titanium Disulphide, TiS_2, is obtained by passing a mixture of titanium tetrachloride vapour and sulphuretted hydrogen through an ignited tube, and forms large brass-yellow, lustrous scales, closely resembling mosaic gold. It burns when ignited in the air, yielding titanium dioxide and sulphur dioxide.

Titanium Sesquisulphide, Ti_2S_3, is formed by passing a mixture of moist sulphuretted hydrogen and carbon disulphide vapour over titanium dioxide heated to bright redness,[1] or by igniting the disulphide in a current of an indifferent gas;[2] it forms a greenish-black or grey powder. It is stable towards dilute solutions of acids and alkalis, but forms green solutions of unknown composition in concentrated sulphuric and nitric acids.

Titanium Monosulphide, TiS, is prepared by heating either of the foregoing compounds in a current of hydrogen and is a lustrous substance resembling bismuth.

Titanous Sulphate, $TiSO_4$, is formed when metallic titanium is dissolved in sulphuric acid and the solution evaporated to dryness.

Titanium Sesquisulphate, $Ti_2(SO_4)_3,8H_2O$, is obtained by dissolving the metal in dilute sulphuric acid. The violet solution on concentration assumes a fine blue lustre and deposits small tufts of crystals (Glatzel).[3] By repeated evaporation *in vacuo* of a solution of titanium trichloride with dilute sulphuric acid, violet crystals of the composition $3Ti_2(SO_4)_3,H_2SO_4,25H_2O$ are obtained, and the same compound is formed also by the electrolysis of a solution of titanium tetrachloride in concentrated sulphuric acid. This substance forms a violet solution in water, and on repeated evaporation with concentrated sulphuric acid in absence of air, yields the anhydrous sesquisulphate as an insoluble, green, crystalline powder (Stähler). Titanium sesquisulphate is decomposed by heat into sulphur dioxide, sulphur trioxide, and titanium dioxide. It forms an alum with cæsium sulphate, $Cs_2SO_4,Ti_2(SO_4)_3,24H_2O$, which crystallises in cubes, and a similar alum with rubidium sulphate,[1] whilst a double sulphate, $Ti_2(SO_4)_3,Na_2SO_4,5H_2O$, has also been prepared.[2] The violet acid salt forms with rubidium and ammonium sulphates the compounds $3Ti_2(SO_4)_3,Rb_2SO_4,24H_2O$ and

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[1] Thorpe, *Journ. Chem. Soc.*, 1885, 47, 491.

[2] von der Pfordten, *Annalen*, 1886, 234, 290.

[3] Compare Stähler, *Ber.*, 1905, 38, 2619.

$$3Ti_2(SO_4)_3,(NH_4)_2SO_4,18H_2O \text{ (Stähler).}$$

Normal Titanium Disulphate, $Ti(SO_4)_2,3H_2O$, is formed by the oxidation of the sesquisulphate with nitric acid, and on evaporation remains as a transparent, yellowish, deliquescent, amorphous mass. The sulphate forms double salts, such as $K_2SO_4,Ti(SO_4)_2,3H_2O$, $Ti(SO_4)_2,CaSO_4$, etc.[3]

Basic Titanium Sulphate, $(TiO)SO_4$, is obtained as a hard white mass by dissolving dry titanic acid in boiling sulphuric acid and evaporating,[4] whilst crystals of $(TiO)SO_4,5H_2O$ are obtained by boiling titanic acid with alcoholic sulphuric acid and evaporating.[5] Several other basic sulphates have been prepared[6] by heating titanium dioxide with sulphuric acid in sealed tubes at different temperatures.

TITANIUM AND NITROGEN.

379 Titanium is one of the elements which very readily combine with nitrogen, and two compounds of these two elements are known.

Titanium Mononitride, TiN, is obtained by heating titanium dioxide very strongly in the electric furnace in presence of nitrogen. A better method[7] is to heat titanium dioxide in a porcelain boat for six hours at 1400–1500° in a stream of ammonia. It is a bronze-yellow mass which has a specific gravity of 5·18 and is hard enough to scratch rubies and cut diamonds.[1]

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[1] Piccini, *Gazz.*, 1895, 25, [2], 542; *Zeit. anorg. Chem.*, 1898, 17, 355.

[2] Spence and Son, German Patent, 149602 (1904).

[3] Weinland and Kühl, *Zeit. anorg. Chem.*, 1907, 54, 253.

[4] Merz, *J. pr. Chem.*, 1866, 99, 157.

[5] Rosenheim and Schütte, *Zeit. anorg. Chem.*, 1901, 26, 239.

[6] Blondel, *Bull. Soc. Chim.*, 1899, [3], 21, 262.

[7] Ruff, *Ber.*, 1909, 42, 900.

Titanium Nitride, Ti_3N_4.—When the compound $TiCl_4,4NH_3$ is heated a copper coloured compound is obtained,[2] which was regarded as the element until Wohler,[3] showed that it contained nitrogen and gave it the formula Ti_3N_4. Wohler also prepared a dark blue compound with a coppery sheen to which he gave the formula TiN_2. It has been shown by Schneider[4] that the former substance contains oxygen and the latter does not exist. The tetranitride has been prepared by Ruff and Treidel[5] as follows: The compound $TiBr_4,8NH_3$ is washed with liquid ammonia to form an orange-coloured substance of the approximate composition $2Ti(NH_2)_4,TiBr_4,8NH_3$. The compound is then treated with a solution of an equivalent amount of potassamide in liquid ammonia, when monopotassium titanium di-imide, $Ti(NH)NK$, and titanic nitride are formed. The nitride has a brown colour and is decomposed by water into ammonia, and by heat into TiN and nitrogen.

TITANIUM AND CARBON.

380 *Titanium Carbide*, TiC, is prepared by fusing titanium dioxide with an excess of carbon, or with calcium carbide in the electric furnace, and is thus obtained as a mass having a crystalline fracture, and a specific gravity of 4·25; it is not attacked by hydrochloric acid, is only slowly dissolved by aqua regia, and does not decompose steam at 700°. In other respects it resembles metallic titanium, but burns more readily in oxygen.[6]

Steel-grey crystals of titanium carbide have been obtained from cast iron prepared from titaniferous ores.[7] Titanium carbide is used for making arc lamp electrodes.

Titanium Cyanonitride.—When iron ores containing titanium are reduced in the blast-furnace small brilliant copper-coloured cubes, which are hard enough to scratch glass and are almost infusible, are found in cavities both of the slag and of the metal. A mass containing as much as 80 lb. has been found in a single blast-furnace in the Harz. This substance was examined l Wollaston in 1822 and believed by him to be metallic titanium but Wöhler, in 1849 showed that it contained nitrogen a cyanogen, and gave to it the formula $Ti(CN)_2,3Ti_3N_2$. H likewise obtained it artificially[2] by heating a mixture of ferr cyanide of potassium and titanium dioxide in a well-close crucible at a temperature sufficient to melt nickel. Titaniu cyanonitride can also be prepared by heating to whiteness mixture of titanium dioxide and charcoal in a tube of gas carbo in a stream of dry nitrogen (Deville and Wöhler).[3] A thir method of preparation is to fuse potassium cyanide in the vapou of titanium tetrachloride (Wöhler). It has a specific gravit of 5·28, and is attacked only by a mixture of nitric and hydro fluoric acids. When ignited in a current of steam it is decompose as follows:

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[1] Moissan, *Compt. rend.*, 1895, **120**, 290.

[2] Liebig, *Pogg. Ann.*, 1830, **21**, 259.

[3] *Annalen*, 1850, **73**, 34.

[4] *Zeit. anorg. Chem.*, 1895, **8**, 81.

[5] Ruff and Treidel, *Ber.*, 1912, **45**, 1364.

[6] Moissan, *Compt. rend.*, 1895, **120**, 290; 1897, **125**, 839.

[7] Shimer, *Chem. News*, 1887, **55**, 156.

$$Ti(CN)_2,3Ti_3N_2 + 20H_2O = 2HCN + TiO_2 + 6NH_3 + 10H_2.$$

Chlorine also decomposes this substance at a red heat, titanium tetrachloride and a volatile sublimate consisting of a compound of titanium tetrachloride and cyanogen chloride being formed. When fused with potash ammonia is given off, potassium titanate being produced.

DETECTION AND ESTIMATION OF TITANIUM.

381 Titanium is distinguished from tin inasmuch as its oxides are not reduced to the metallic state when heated on charcoal before the blowpipe. With microcosmic salt titanium dioxide yields a colourless bead in the outer flame, but in the inner flame the bead is yellow whilst hot and assumes a violet colour on cooling. According to Riley, the delicacy of this reaction is increased by melting metallic zinc in the microcosmic bead heated on charcoal, a distinct coloration being then obtained when the zinc is burnt away, even with minute quantities of titanium. When fused in the microcosmic bead with addition of a small quantity of an iron salt in the reducing flame, a bright-red bead is obtained. Titanium compounds do not colour the gas-flame, but both the spark and the arc spectrum show an enormous number of bright lines, chiefly in the blue and green, which have been carefully mapped by Thalén and others.

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[1] *Phil. Trans.*, 1823, **113**, 17.
[2] *Annalen*, 1850, **73**, 34; **74**, 212.
[3] *Ibid.*, 1857, **103**, 230.

Metallic zinc placed in a hydrochloric acid solution of titanic acid evolves hydrogen and the liquid assumes a violet-blue colour; a dark violet precipitate is formed if the solution be not too dilute, and this gradually turns white by oxidation. The violet-blue solution when diluted with water assumes a rose-colour, and this reaction serves for the detection of small quantities of titanium. Sodium thiosulphate when boiled with a nearly neutral solution of a titanate precipitates the whole of the titanic acid, and this reaction serves as a means of separating titanium from iron and the metals of the group.

In order to remove silica, when present, the mixture is evaporated with hydrofluoric acid, the silicon being expelled as silicon tetrafluoride.

Titanium is always estimated gravimetrically in the form of titanium dioxide, this being thrown down from its solutions in acids by ammonia, or by saturating with sulphur dioxide and boiling. Titanium may also be estimated volumetrically by reducing titanium dioxide to titanium sesquioxide by means of zinc in an acid solution and subsequently oxidising with standard permanganate.

Atomic Weight of Titanium.—The atomic weight of titanium was first determined by Rose[1] in 1829 by decomposing titanium tetrachloride with water, weighing the titanic acid formed and estimating the chlorine in the filtrate, the number found being 47·72. A redetermination was made in 1885 by Thorpe,[2] who analysed pure titanium tetrachloride and tetrabromide, the amount of silver required for complete precipitation of the halogen, the amount of silver halide formed, and the quantity of titanium dioxide yielded by each being ascertained; the average of the results of the six series of experiments gave the number 48·1, which is at present (1922) adopted.

ZIRCONIUM. $Zr = 90·6$. At. No. 40.

382 In 1789 Klaproth found a new earth in the mineral zircon, to which he gave the name of zirconia. He discovered in 1795 that the same earth was contained in hyacinth, a mineral found in Ceylon, and he thus ascertained the truth of Werner's previous supposition that these two minerals were identical. Zircon and hyacinth possess the formula $ZrSiO_4$, and are more or less coloured by ferric oxide. Zirconium is found in a few other rare minerals,

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[1] *Pogg. Ann.*, 1829, 15, 145.

[2] *Journ. Chem. Soc.*, 1885, 47, 108.

and occurs in appreciable quantities in Norwegian gradite, with thoria and several of the rare earths.[1]

The metal zirconium was first obtained by Berzelius in the form of an iron-grey powder by heating potassium zirconofluoride with potassium. The metal can also be obtained, according to Troost, by passing the vapour of zirconium chloride, $ZrCl_4$, over heated sodium. The ignited amorphous metallic powder thus obtained is so finely divided that it passes through the pores of filter paper, but it assumes a metallic lustre under the burnisher. The amorphous metal may also be prepared by heating zirconia with magnesium powder,[2] and thus prepared it has a velvet-black appearance like wood charcoal.

Wedekind[3] has obtained a metal containing 99·09 per cent. of zirconium. He heats an intimate mixture of ZrO_2 and calcium shavings in an evacuated iron vessel. When the reaction is completed the contents of the tube are treated successively with water, acetic acid, dilute hydrochloric acid, and water, all the operations being conducted in absence of air. The residual powder is then washed with acetone and dried *in vacuo* at 250–300°; finally, at a temperature of 800–1000°, the powder sinters, but does not melt; it exhibits a mirror-like brilliancy on polishing. Zirconium of 99·3 per cent. purity has been obtained by the action of sodium on potassium zirconofluoride by the same method[4] as that described for titanium (*q.v.*).

Crystallised zirconium was first obtained by heating potassium zirconofluoride with aluminium at the temperature of melting iron; it is, however, best prepared by heating zirconia in the electric furnace with an insufficient quantity of carbon for its complete reduction, and is thus obtained as a metallic button containing some zirconia but free from carbon and nitrogen. It may also be obtained by heating the carbide with zirconia in a similar manner,[5] or by heating potassium zirconofluoride with magnesium in the electric furnace.[6]

Crystallised zirconium forms broad, apparently monoclinic, plates, has a specific gravity of 4·08 at 15°,[1] and is hard enough to scratch glass and rubies. It is only very slowly oxidised in the air even at a white heat, but burns in the oxy-hydrogen flame, and yields the tetrachloride when heated to dull redness in chlorine or hydrogen chloride. It is also dissolved by caustic potash with evolution of hydrogen. It is only slowly attacked by acids, with the exception of hydrofluoric, even on heating, but is rapidly oxidised by aqua regia. The amorphous metal readily takes fire in the air on warming.

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[1] Phipson, *Chem. News*, 1896, **73**, 145. See also Marden and Rich, *Bur. Mines Bull.*, 1921, **186**.

[2] Phipson, *Compt. rend.*, 1865, **61**, 745; *Chem. News*, 1906, **93**, 110; Winkler, *Ber.*, 1890, **23**, 2664.

[3] *Annalen*, 1913, **395**, 149; compare also Weiss and Neumann, *Zeit. anorg. Chem.*, 1910, **65**, 248.

[4] Podszus, *Zeit. anorg. Chem.*, 1917, **99**, 123. See also Marden and Rich, *J. Ind. Eng. Chem.*, 1920, **12**, 651.

[5] Moissan, *Compt. rend.*, 1893, **116**, 1222; Troost, *ibid.*, 1428.

[6] Wedekind, *Zeit. Elektrochem.*, 1904, **10**, 331.

ZIRCONIUM COMPOUNDS.

383 *Zirconium Oxide or Zirconia*, ZrO_2.—In order to prepare this oxide zircon is ignited and then quenched in water. The powdered mineral is mixed with three to four times its weight of acid potassium fluoride, and gently heated in a platinum vessel until all moisture has been driven off. The platinum crucible is then placed in a Hessian one, and both are well covered and exposed for two hours to the strongest heat of a wind furnace. The porcelain-like mass thus obtained is boiled with water containing hydrofluoric acid, and the insoluble potassium silicofluoride filtered off. On cooling the solution, crystals of potassium zirconofluoride are deposited, and these are purified by recrystallisation. The pure salt is then heated with sulphuric acid until all the hydrofluoric acid is driven off; the residue is dissolved in water, and the zirconia precipitated in the cold by ammonia.[2]

In order to avoid the use of hydrofluoric acid, the very finely powdered zircon may be treated as follows. It is first fused with hydrogen potassium sulphate and the fused mass repeatedly boiled out with water containing sulphuric acid, when a residue of basic zirconium sulphate, $4ZrO_2,3SO_3,14H_2O$, is obtained, which is next fused with caustic soda in a silver basin. This is then lixiviated with water, the residual zirconia, which contains soda, washed with hot water and dissolved in hot concentrated sulphuric acid, the solution filtered and precipitated with ammonia.[3] The precipitate thus obtained consists of zirconium hydroxide, which readily parts with its water on heating. When heated at 140–200° it has the composition ZrO_2,H_2O, and is known as zirconic acid. A hydrated oxide containing less water than this is obtained by repeatedly boiling zirconium oxychloride

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[1] Meyer, *Monatsh.*, 1899, 20, 793. [2] Homberger, *Annalen*, 1876, 181, 232.
[3] Franz, *Ber.*, 1870, 3, 58.

with water and drying the precipitate at 100°; this has been called metazirconic acid.[1] According to van Bemmelen,[2] *however, these substances are probably not true hydroxides, but colloidal zirconia, containing water in the form of a hydrogel.* The hydroxide is slightly soluble in water, and colours yellow turmeric paper brown. When precipitated and washed in the cold, it is easily soluble in dilute acids; if, however, it be precipitated from a hot solution, or washed with boiling water, it is soluble only in concentrated acids. When heated to incipient redness it is converted into zirconia with evolution of heat. The oxide thus obtained has the specific gravity[3] 5·489, and is only slightly soluble even in hydrofluoric acid, but dissolves on heating in a mixture of two parts of sulphuric acid and one part of water. An hydroxide of the formula $Zr_5O_8(OH)_7$, which gives rise to a chloride, $Zr_5O_8Cl_4,22H_2O$, and a sulphate, $Zr_5O_8(SO_2)_2,xH_2O_4$, has been described by Rodd.[4]

Zirconia can be obtained in the crystalline state in the form of tetragonal prisms isomorphous with cassiterite and rutile and having a specific gravity of 5·71.[5] For this purpose, the amorphous oxide is fused with borax in a porcelain furnace, the fused residue being boiled out with sulphuric acid.

Pure zirconia melts at 3000°, and the fused product has a specific gravity 5·89. The linear coefficient of expansion is 0·00000084, nearly the same as that of fused quartz.

Zirconia is employed in the preparation of rods for the Nernst electric lamp. Crucibles, etc., can be made by mixing zirconia with 10 per cent. of magnesia. Crucibles made from zirconia mixed with 1–3 per cent. of yttria[6] do not soften until 2400°. Platinum can be melted in such crucibles with the oxy-hydrogen flame. Quartz can also be melted without destroying the crucible.[7]

Zirconia, like the dioxides of the other metals of this group, acts as an acid-forming oxide, and yields salts corresponding to the metasilicates and metatitanates.

Sodium Zirconate, Na_2ZrO_3, obtained by fusing the oxide with sodium carbonate, forms a crystalline mass which is decomposed by water with separation of zirconia. When heated with an excess of sodium carbonate to whiteness the salt Na_4ZrO_4 is produced. This is again decomposed by water with formation of hexagonal tablets having the composition $Na_2Zr_8O_{17},12H_2O = Na_2O,8ZrO_2,12H_2O$.

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[1] Ruer, *Zeit. anorg. Chem.*, 1905, **43**, 282.

[2] *Zeit. anorg. Chem.*, 1906, **49**, 125.

[3] Venable and Belden, *J. Amer. Chem. Soc.*, 1898, **20**, 273.

[4] *Journ. Chem. Soc.*, 1917, **111**, 396.

[5] Nordenskiold, *Pogg. Ann.*, 1861, **114**, 612.

[6] Ruff and Lauschke, *Zeit. anorg. Chem.*, 1916, **97**, 73.

[7] Weiss and Lehmann, *Zeit. anorg. Chem.*, 1909, **65**, 178.

Zirconium Sesquioxide,[1] Zr_2O_3, is prepared as a green powder by the combustion of zirconium hydride. On ignition in air, it is converted into the dioxide.

Zirconium Peroxide, $Zr_2O_5,9H_2O$, is obtained as a white powder when hydrogen peroxide is added to a solution of zirconium sulphate. Under certain conditions a hydrated oxide, $ZrO_3,5H_2O$, is formed,[2] and this when treated with excess of hydrogen peroxide and an alkali hydroxide is stated to form the alkali salts of *perzirconic acid,*[3] $H_4Zr_2O_{11}$.

Zirconium and Hydrogen.—When zirconia is heated with magnesium powder in a current of hydrogen the latter is absorbed, the product containing zirconium hydride, ZrH_2, together with zirconia and perhaps a lower oxide.[4] The hydride is also formed when hydrogen acts on the metal at a red heat.[5] It burns in the air to form the sesquioxide.

Zirconium Fluoride, ZrF_4, is obtained by heating zirconia with acid ammonium fluoride. The residual mass is easily soluble in water containing hydrofluoric acid, and crystallises in glistening, triclinic tablets having the composition $ZrF_4,3H_2O$.

According to Chauvenet, the hydrate, $ZrF_4,3H_2O$, is really $ZrOF_2,2HF,2H_2O$, for on heating to 140° water is lost and $ZrOF_2,2HF$ left, whilst at higher temperatures the compound $ZrOF_2$, is formed.[6] The anhydrous compound sublimes and forms small, highly refractive prisms with a density 4·433. It dissolves slightly in water, and when the solution is warmed, zirconium hydroxide is precipitated. It combines with liquid ammonia to form $5ZrF_4,2NH_3$.

Zirconium fluoride forms a series of double salts with other fluorides which are isomorphous with the corresponding silicofluorides, titanifluorides, and stannifluorides.

Potassium Zirconofluoride, K_2ZrF_6, is obtained by igniting zircon with acid potassium fluoride or by pouring a solution of potassium fluoride into an excess of zirconium fluoride solution. It crystallises in small, acute, rhombic prisms, and dissolves at 2° in 128, at 15° in 71, and at 100° in 4 parts of water.

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[1] Weiss and Neumann, *Zeit. anorg. Chem.*, 1909, **65**, 248.

[2] Bailey, *Journ. Chem. Soc.*, 1886, **49**, 481.

[3] Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 609.

[4] Winkler, *Ber.*, 1891, **24**, 888.

[5] Wedekind, *Ann.*, 1913, **395**, 149; Weiss and Neumann, *Zeit. anorg. Chem.*, 1910, **65**, 248.

[6] *Compt. rend.*, 1917, **164**, 727.

When zirconium hydroxide is dissolved in the smallest quantity of hydrofluoric acid and the liquid is poured into a concentrated solution of neutral potassium fluoride, the salt K_2ZrF_6,KF is precipitated, and crystallises from boiling water in fine needles.

If sodium fluoride and zirconium fluoride are mixed in any proportion, the salt $Na_2ZrF_6,4NaF$ is produced. It forms small, monoclinic crystals which dissolve in 258 parts of water at 18°, and at 100° in about 60 parts of water.

Ammonium salts, corresponding to the salts of potassium, and other double fluorides,[1] are known.

Zirconium Chloride, $ZrCl_4$, is obtained by passing chlorine gas over a heated mixture of zirconia and charcoal, by the action of chlorine or hydrogen chloride on the heated metal, when it is obtained as a white, crystalline sublimate by heating the dioxide with phosphorus pentachloride at 190° in a sealed tube, and best of all by heating the dioxide in a stream of chlorine and carbon tetrachloride at 800°. It may be recrystalliesd from hydrochloric acid, but it is doubtful whether it has ever been obtained in this way free from the oxychloride. Zirconium chloride forms with ammonia the compounds[2] $ZrCl_4,8NH_3$ and $ZrCl_4,3NH_3$. On addition of water to the chloride heat is evolved, and zirconium oxychloride, $ZrOCl_2$, is formed, which remains dissolved in the acid solution. The same compound is obtained by dissolving zirconium hydroxide in dilute hydrochloric acid, and on evaporation crystallises out in prismatic needles belonging to the tetragonal system, and having the composition $ZrOCl_2,8H_2O$.[3] These are readily soluble in water, have an astringent taste, and when heated to 50° lose water, forming more basic oxychlorides, whilst by treatment with concentrated hydrochloric acid crystals of $ZrOCl_2,6H_2O$ and $ZrOCl_2,3H_2O$ have been obtained.[4]

Zirconium Bromide, $ZrBr_4$, is prepared in a similar way to the chloride, and forms a white, crystalline powder which is easily volatilised at the temperature of the gas flame. In contact with moist air or water it forms zirconium oxybromide, $ZrOBr_2$, which crystallises in needles, and may also be prepared by evaporating a solution of the hydroxide in hydrobromic acid, when $ZrOBr_2,8H_2O$ separates out.[1] With ammonia,[2] zirconium bromide gives the compounds $ZrBr_4,4NH_3$ and $ZrBr_4,10NH_3$. A number of oxybromides of the same types as the oxychlorides are known.

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[1] See also Wells and Foote, *Zeit. anorg. Chem.*, 1895, **10**, 434; *Amer. J. Sci.*, 1897, **3**, 461.

[2] Stähler and Denk, *Ber.*, 1905, **38**, 2611. Compare Matthews, *J. Amer. Chem. Soc.*, 1898, **20**, 815.

[3] Weibull, *Ber.*, 1887, **20**, 1394.

[4] Venable and Baskerville, *J. Amer. Chem. Soc.*, 1898, **20**, 321.

Zirconium Iodide, ZrI_4, is obtained by passing hydrogen iodide over zirconium or the carbide at a bright red heat. According to Dennis and Spencer,[3] it is a white, crystalline body which is insoluble in water and acids; Stähler and Denk,[4] however, state that it dissolves in water and acids, the aqueous solution depositing colourless crystals of the *oxyiodide*, $ZrOI_2,8H_2O$.

Zirconium Sulphide.—When metallic zirconium and sulphur are heated together in a current of hydrogen they combine with evolution of heat to form a cinnamon-brown powder, which assumes a metallic lustre under the burnisher. This is not attacked by most of the dilute acids, but dissolves slowly in aqua regia and readily in hydrofluoric acid. When fused with potash, zirconia and potassium sulphide are formed.

Zirconium Sulphate, $Zr(SO_4)_2$, is obtained by dissolving the oxide or hydroxide in sulphuric acid, evaporating, and heating nearly to redness. It is a white mass which dissolves slowly but completely in cold, and quickly in hot water. Hydrated crystals are obtained by concentrating a solution which contains free acid, and these swell up on heating, like alum. The salt decomposes at a red heat, leaving a residue of pure zirconia. The behaviour of zirconium sulphate in solution[5] is best represented by the formula $(ZrO)SO_4,H_2SO_4$, whilst the crystalline hydrated salt is $(ZrO)SO_4,H_2SO_4,3H_2O$, and not $Zr(SO_4)_2,4H_2O$ as was formerly thought. If its solution be saturated with zirconium hydroxide a basic salt, $Zr(SO_4)_2,ZrO_2$ or $(ZrO)SO_4$, is formed, and this is obtained on evaporation as a hydrated mass. If the normal salt be precipitated with alcohol an insoluble salt, $Zr(SO_4)_2,2ZrO_2$, is thrown down. A large number of similar basic sulphates have been described by Chauvenet[1] and Rodd.[2]

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[1] Rosenheim and Frank, *Ber.*, 1907, 40, 803.

[2] Matthews, *J. Amer. Chem. Soc.*, 1898, 20, 839; Stähler and Denk, *Ber.*, 1905, 38, 2611.

[3] *J. Amer. Chem. Soc.*, 1896, 18, 673.

[4] *Ber.*, 1904, 37, 1137.

[5] Ruer, *Zeit. anorg. Chem.*, 1904, 42, 187; Ruer and Levin, *ibid.*, 1905, 46, 449; Rosenheim and Frank, *Ber.*, 1907, 40, 803.

Zirconium and Nitrogen.—The nitride, Zr_2N_3, is obtained by heating zirconium chloride to redness in a current of dry ammonia,[3] and also by heating zirconia and magnesium in a loosely-covered crucible.[4] It is a brownish-green, crystalline powder which oxidises with incandescence when gently heated in air (Wedekind). A nitride of the formula Zr_3N_8 is formed when the compound $ZrCl_4,8NH_3$ is heated to redness in nitrogen (Matthews). Bruère and Chauvenet[5] are unable to obtain the compound Zr_3N_8, but always obtain Z_3N_4, on heating ammonia derivatives of zirconium chloride.

Zirconium Nitrate, $Zr(NO_3)_4$, is obtained as a yellow, gummy mass by dissolving the hydroxide in nitric acid and evaporating at a moderate heat. If the solution be evaporated *in vacuo* over caustic soda and phosphorus pentoxide, extremely hygroscopic crystals of $Zr(NO_3)_4,5H_2O$ separate out.[6] The existence of normal zirconium nitrate has been questioned by Chauvenet,[7] who finds that the concentration of a solution of this salt always leads to the loss of nitric acid and the separation of the basic salts, $ZrO(NO_3)_2,2H_2O$, at ordinary temperatures, and $ZrO(NO_3)_2,3{\cdot}5H_2O$, at temperatures below 10°. A number of other basic nitrates also exist.

Zirconium Boride, Zr_3B_4, has been prepared by heating in the electric furnace a mixture of zirconium and boron;[8] it forms a steel-grey mass, consisting of microscopic crystals, and has the specific gravity 3·7.

Zirconium Carbides.—Zirconium combines with carbon to form two carbides having the composition ZrC_2 and ZrC. The *dicarbide* is obtained by heating zirconia with an excess of carbon in the electric furnace and has a metallic appearance and brilliant fracture, and is not decomposed by water even on heating. The *monocarbide* is prepared in a similar manner, but the mixture of zirconia and carbon is placed in a carbon tube closed at one end, which is then heated in the electric furnace.

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[1] *Compt. rend.*, 1917, **164**, 864, 946; **165**, 25; 1918, **167**, 24, 126.

[2] *Journ. Chem. Soc.*, 1917, **111**, 396.

[3] Matthews, *J. Amer. Chem. Soc.*, 1898, **20**, 840.

[4] Wedekind, *Zeit. anorg. Chem.*, 1905, **45**, 385.

[5] *Compt. rend.*, 1918, **167**, 201.

[6] Rosenheim and Frank, *Ber.*, 1907, **40**, 803.

[7] Chauvenet and Nicolle, *Compt. rend.*, 1918, **166**, 781, 821.

[8] Tucker and Moody, *Journ. Chem. Soc.*, 1902, **81**, 14.

It has a grey colour and metallic lustre, and is hard enough to scratch quartz. It is permanent in the air and is not decomposed by water, but burns brilliantly in oxygen.[1]

Zirconium Silicide, $ZrSi_2$.—This compound is obtained by heating a mixture of potassium zirconofluoride, aluminium, sulphur, and sand, the whole being covered with a layer of magnesium powder.[2] It forms small steel-grey crystals having the specific gravity 4·88 at 22°.

Silicates of Zirconium.—Of these, zircon or hyacinth, $ZrSiO_4$, is the most important. It occurs in crystalline rocks, especially in granular limestone, schist, gneiss, syenite, and granite. The chief localities are in alluvial sands in Ceylon, the Urals, in the Isle of Harris, in Greenland, in the gold districts of Australia, and in many places in North America. Zircon crystallises in tetragonal prisms and pyramids (Fig. 182), having an adamantine lustre; they are colourless in the pure state. Usually, however, zircon is coloured red or yellow by ferric oxide. The colourless and smoke-coloured varieties are termed jargon. This variety exhibits a peculiar absorption spectrum, from which Sorby concluded that it contained a new element; to this he gave the name of jargonium, but subsequently he found that these lines were caused by the presence of uranium oxide. An artificial jargon yielded a similar spectrum, though neither uranium nor zirconium compounds do so.[3]

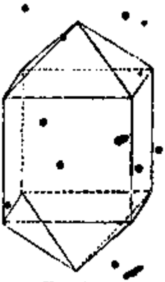

Fig. 182.

Detection and Estimation of Zirconium.

384 The reactions of the zirconium salts are very similar to those of the metals contained in cerite and gadolinite. A reaction of zirconium by which it is distinguished from the cerium metals is the formation of a basic potassium zirconium sulphate, insoluble in water and hydrochloric acid. This salt is obtained by adding a hot solution of potassium sulphate to a concentrated solution of a zirconium salt. This reaction also serves to separate zirconium from titanium, tantalum, and columbium. Another method of separating zirconium from the metals of the

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[1] Moissan, *Compt. rend.*, 1893, **116**, 1222; 1896, **122**, 651.

[2] Hönigschmid, *Compt. rend.*, 1906, **143**, 224.

[3] *Chem. News*, 1870, **21**, 73.

cerium and iron groups is to boil the solution with sodium thiosulphate; when zirconium alone is precipitated as the thiosulphate; this on washing and heating leaves a residue of zirconia.

Titanic acid and thoria are also precipitated together with the zirconia by sodium thiosulphate. In order to separate these, ammonium oxalate is added to the hydrochloric acid solution, when the thoria is thrown down. Ammonium carbonate is now added to the filtered liquid, when, in the presence of the oxalate, only titanic acid is precipitated, the zirconia remaining in solution (Hermann). Zirconium can readily be separated from iron, titanium, etc., by means of hydrogen peroxide; this precipitates it quantitatively from solutions of the sulphate as the hydrated peroxide (Bailey).

The spectrum of zirconium has been mapped by Thalén, and contains characteristic lines in the red and blue.

Atomic Weight of Zirconium.—The first accurate determination of the atomic weight of zirconium was that of Marignac,[1] who from the analysis of potassium zirconofluoride obtained the number 90·03. Bailey,[2] from the weight of zirconia yielded by a known quantity of pure zirconium sulphate, found the number 90·65, whilst Venables,[3] who estimated the zirconia obtained by heating the oxychloride, $ZrOCl_2,3H_2O$, found the number 90·78. A more recent determination made by the nephelometric method from the ratio $4Ag : ZrCl_4$ gives the value 91·76.[4] The atomic weight now (1922) adopted is 90·6.

HAFNIUM. At. No. 72.

Thomsen in 1895 and Bury[5] in 1921 suggested on chemical grounds that the missing element immediately preceding tantalum in the periodic system should be a tetravalent homologue of zirconium. Bohr has drawn the same conclusion from his theory of atomic structure (p. 79). These views have now received considerable confirmation from the recently reported discovery by Coster and Hevesy,[6] using the method of *X*-ray spectroscopy (p. 72), of a new element, of atomic number 72, in numerous zirconium minerals, in one of which it appears to be present to the extent of at least 1 per cent. "It seems to be very probable that ordinary zirconium contains at least from 0·01 to 0·1 per cent. of the new element. Especially the latter circumstance proves that the element 72 is chemically homologous to zirconium. Experiments are in progress to isolate the new element and to determine its chemical properties. For the new element we propose the name Hafnium (Hafniæ = Copenhagen)."

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[1] *Ann. Chim. Phys.*, 1860, [3], 60, 257.

[2] *Proc. Roy. Soc.*, 1890, 46, 74.

[3] *J. Amer. Chem. Soc.*, 1898, 20, 119.

[4] Venables and Bell, *J. Amer. Chem. Soc.*, 1917, 39, 1598.

[5] *J. Amer. Chem. Soc.*, 1921, 43, 1602.

[6] *Nature*, 1923, 111, 79.

The atomic weight of this element may be expected to be in the neighbourhood of 178.

This discovery throws doubt on the claim of Urbain's rare-earth element, Celtium (p. 829), to the position 72, though Dauvillier[1] has recently supported this claim by means of X-ray spectroscopy.

THORIUM. Th = 232·4. At. No. 90.

385 In the year 1815 Berzelius believed that he had found in several Swedish minerals a new earth to which he gave the name of thoria, but on further examination the substance turned out to be basic phosphate of yttrium. On the other hand, in 1828,[2] he discovered a distinct earth in a mineral from the island of Lövön, in Norway, now termed thorite, and to this the name of thoria was given, as it agreed in many of its properties with the substance previously so named. Besides being found in thorite, this substance was discovered in other rare minerals; thus by Wöhler in pyrochlor, by Bergman and others in orangite, and by Karsten in monazite, a phosphate of cerium and lanthanum which contains 4–18 per cent. of thoria. Another source of thoria is the mineral euxinite from Arendal, in which this earth was discovered by Mosander and Chydenius, and it has also been found in Norwegian granite.[3] More recently it has been discovered in a mineral called thorianite occurring in Ceylon, which contains 70–80 per cent. of thoria, along with 11–15 per cent. ($UO_2 + UO_3$), 2–3 per cent. of lead, and varying amounts of metals of the cerium and ytterbium group and SiO_2 and CaO.[4] It also contains helium, and when heated to redness evolves 9 c.c. of this gas per 1 gram.[5]

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[1] *Compt. rend.*, 1922, **174**, 1347.

[2] *Pogg. Ann.*, 1829, **16**, 385.

[3] Phipson, *Chem. News*, 1896, **73**, 145.

[4] Dunstan, *Nature*, 1904, **69**, 510; Dunstan and Blake, *Proc. Roy. Soc.*, 1905, **76**, [*A*], 253; Dunstan and Jones, *Proc. Roy. Soc.*, 1906, **77**, [*A*], 546.

[5] Ramsay, *J. Chim. Phys.*, 1905, **3**, 617.

The following table gives the composition of some of these minerals.[1]

Thorite from Lövön.		Thorianite.		Monazite from Ilmengebirge.	
SiO_2	19.31	ThO_2	78.86	P_2O_5	28.50
ThO_2	58.91	UO_2	6.03	ThO_2	17.95
UO_3	1.64	UO_3	9.07	SnO_2	2.10
Fe_2O_3	3.46	CeO_2 La_2O_3 Di_2O_3	1.02	Ce_2O_3	26.00
Mn_2O_3	2.43			La_2O_3	23.40
CuO	2.62			MnO	1.86
MgO	0.36	PbO	2.59	CaO	1.68
K_2O	0.15	Fe_2O_3	0.46		
Na_2O	0.11	CaO	1.13		101.49
PbO	0.82	He	0.39		
SnO_2	0.01	P_2O_5	trace		
Al_2O_3	0.06	Insol. in HNO_3	0.20		
H_2O	9.66				
	99.54		99.75		

Thorium occurs also in other minerals containing the metals of the cerium group, as gadolinite and orthite. In one of these minerals Bahr believed he had found another new metal, to which he gave the name wasium, but he afterwards convinced himself that this substance is identical with thorium.[2]

Doubts have been put forward as to the individuality of thorium, and Baskerville,[3] from experiments on the fractional distillation of the chloride in a current of chlorine, concludes that it contains two other elements to which he gives the names berzelium and carolinium. The work of other investigators, however, does not confirm this result, but points to the uniform nature of thorium.[4]

At the present time thorium compounds are prepared on the manufacturing scale, as they form the chief constituent of the mantles employed for the Welsbach incandescent gas-burner; they are put on the market chiefly in the form of crude thorium nitrate which contains also the nitrates of zirconium and the cerite earths. Thorite is the most convenient raw material, but is not found in sufficient quantity, and the crude material mostly employed is the Brazilian or American monazite sand, which has been formed by disintegration of the rock containing the mineral monazite.

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[1] See Schilling, *Zeit. angew. Chem.*, 1902, **15**, 921, where a *résumé* of the analyses of orangite and thorite is given.

[2] *Annalen*, 1864, **132**, 227.

[3] Baskerville, *J. Amer. Chem. Soc.*, 1901, **23**, 761; 1904, **26**, 922; *Ber.*, 1905, **38**, 1444. See also Brauner, *Proc. Chem. Soc.*, 1901, **17**, 67.

[4] Meyer and Gumprey, *Ber.*, 1905, **38**, 817; Eberhard, *ibid.*, 826.

Although the process adopted for the preparation on a large scale of thorium nitrate for the incandescent mantle industry is kept secret, the following is a general outline. The powdered monazite sand either from Brazil or Carolina is moderately heated with concentrated sulphuric acid in cast-iron pans. When the reaction is finished the partially solidified product is dissolved in cold water. It is important that at this stage the solution be kept strongly acid, otherwise the phosphates of the metals will be deposited. The undissolved residue of quartz, ferrotitanium, zircon, magnetic oxide of iron, etc., is separated by decantation. The solution is now fractionally neutralised with magnesia. Owing to thorium phosphate being the least soluble of the phosphates, the first fraction consists mainly of this.

The crude phosphate is dissolved in concentrated hydrochloric acid, oxalic acid added, when the thorium is precipitated as oxalate, together with small quantities of cerium and ytterbium metals. The well washed precipitate is then treated with warm sodium carbonate solution. The thorium goes into solution with traces of ytterbium metals, but the cerium remains undissolved as the double carbonate. By treatment with alkali hydroxide the hydroxide is precipitated, or the oxalate is reprecipitated by means of hydrochloric acid. In order to remove traces of impurities the oxalate or hydroxide is converted into sulphate with sulphuric acid and the sulphate purified by being several times recrystallised, the salt $Th(SO_4)_2,8H_2O$ crystallising out. In order to prepare the nitrate this salt is boiled with ammonia, by which means the hydroxide is produced. This is well washed, and dissolved in nitric acid. The solution is evaporated to dryness, and heated on the water-bath until on ignition it is found to contain 48 to 49 per cent. of ThO_2, representing the nitrate with practically $4H_2O$.[1]

Metallic thorium is obtained by heating potassium thorium chloride with sodium in an iron cylinder. Thus prepared, it forms microscopic hexagonal tablets, having the colour of nickel, and giving a silver-white streak. It has also been prepared by the action of sodium vapour on the vapour of certain volatile organic compounds of thorium such as the acetylacetonate.[2]

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[1] Boehm, *Chemische Industrie*, 1906, 29, Nos. 17-19; Dieseldorff, *ibid.*, 1906, 29, 411.

[2] Siemens and Halske, German Patent, 133959, 1900. See also Moissan and Hönigschmid, *Ann. Chim. Phys.*, 1906, [8], 8, 182.

According to von Bolton,[1] thorium melts at 1450°, whilst Wartenberg[2] gives 1700° as the melting point. At ordinary temperatures the specific heat is 0·02787. It has a specific gravity of 11·0 (Nilson), and 11·32, but after heating and rolling 12·16 (v. Bolton), and takes fire when heated in the air, burning with a bright flame; it dissolves with difficulty in hydrochloric acid, and is not attacked by aqueous alkalis, but is readily soluble in aqua regia;[3] with nitric acid it first dissolves rapidly, but soon becomes passive. At 450° thorium combines with chlorine, bromine, iodine, and sulphur, with incandescence; at 650° it combines with hydrogen and nitrogen respectively to form the hydride and nitride. Thorium is slightly more electropositive than magnesium, it forms alloys with copper, aluminium, zirconium, tungsten, and nickel. In the case of nickel an intermetallic compound, Th_2Ni, has been isolated. Thorium possesses the property of radioactivity, and this will be discussed in the chapter on this subject.

COMPOUNDS OF THORIUM.

386 *Thorium Dioxide* or *Thoria*, ThO_2, is obtained from thorite or orangite by heating the powdered mineral with a slight excess of sulphuric acid and a little water; the dried mass is powdered, heated to remove excess of sulphuric acid, and the residue carefully dissolved in six to seven parts of ice-cold water. The solution is filtered from silica, and heated to the boiling point with ammonia. The precipitated hydroxides are washed by decantation, dissolved in hydrochloric acid and precipitated with oxalic acid, the precipitate well washed by decantation, and ignited. The thoria thus obtained still contains ceria, yttria, and a little manganese. To obtain pure thoria the product is again dissolved in sulphuric acid, the excess of sulphuric acid removed by careful heating, the powdered salt dissolved in ice-cold water, and the temperature of the solution allowed to rise gradually to 20°. A hydrated sulphate of thorium then separates out as an insoluble precipitate, the other metals remaining in solution, and by repeating the process several times the thorium sulphate may be obtained perfectly pure. It is then precipitated by ammonia and the hydroxide thus obtained ignited.[4]

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[1] *Zeit. Elektrochem.*, 1908, 14, 809.

[2] *Ibid.*, 1909, 15, 33

[3] Nilson, *Ber.*, 1882, 15, 2519, 2537; 1883, 16, 153.

[4] Krüss and Nilson, *Ber.*, 1887, 20, 1665.

Pure thoria is a snow-white powder, which may be obtained in tetragonal crystals, isomorphous with those of cassiterite and rutile, by heating the amorphous powder with borax in a porcelain furnace. They possess a specific gravity of 10·2, and dissolve in sulphuric acid only on long-continued boiling. As already mentioned, thoria forms the chief constituent of the Welsbach incandescent mantles, the other and smaller constituents consisting of more basic oxides, that of cerium being usually employed (see p. 815).

Meta-thorium Oxide is obtained by igniting the oxalate, and its peculiar deportment with volatile acids explains the fact that Bahr believed this to be the oxide of a new metal. It was considered to be Th_3O_5, but has been found to have the empirical formula ThO_2, and, according to Wyrouboff and Verneuil,[1] is a polymerised form of thorium dioxide. If it be treated with hydrochloric acid or nitric acid no apparent action takes place, but if the excess of acid be evaporated on the water-bath, a brownish, semi-transparent residue is left, and this dissolves in water to form a translucent, opalescent liquid which appears milk-white in reflected light, and yields a precipitate with acids. This is due to the fact that the oxide forms salts with these acids without loss of water, and these are soluble in water but not in the acids, and are therefore precipitated again by addition of the acids to the solution. If the solution be treated with ammonia and the precipitate dried at 100°, a compound having the composition $Th_4O_7(OH)$ is obtained and this is insoluble in acids.[2]

Thorium Peroxide, Th_2O_7.—This unstable compound is produced when hydrogen peroxide is added to the sulphate or acetate, and then excess of ammonia added.[3] It forms a gelatinous precipitate which on keeping slowly gives up oxygen, being converted into ThO_3.[4]

Thorium Hydride, ThH_4, is obtained by heating thorium to a dull red heat in hydrogen.[5] It is not acted upon by water, but dissolves in hydrochloric acid with evolution of hydrogen. When heated in air, it decomposes with the evolution of hydrogen. At 390° it has a dissociation pressure of one atmosphere.

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[1] *Compt. rend.*, 1898, **127**, 863; *Zeit. anorg. Chem.*, 1901, **28**, 90; *Ann. Chim. Phys.*, 1905, [8], **6**, 441. See also Stevens, *Zeit. anorg. Chem.*, 1901, **27**, 41.

[2] Cleve, *Bull. Soc. chim.*, 1874, **21**, 115.

[3] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [8], **6**, 441.

[4] Pissarjewski, *Zeit. angew. Chem.*, 1902, **31**, 359.

[5] Matignon and Delépine, *Compt. rend.*, 1901, **132**, 36.

§87 *Salts of Thorium.*—The salts of thorium are colourless, and when soluble possess a strongly astringent taste.

Thorium Fluoride, ThF_4, is obtained by the addition of hydrofluoric acid or a fluoride to a solution of a thorium salt as a gelatinous precipitate which passes into a heavy white powder, $ThF_4,8H_2O$, which loses 4 molecules of water in a vacuum and produces $ThF_4,4H_2O$. At 110° in a current of hydrogen the hydrate, $ThF_4,2H_2O$, is formed, whilst at 250° the whole of the hydrates yield the basic fluoride, $Th(OH)F_3,H_2O$. The oxyfluoride, $ThOF_2$, is formed when $ThF_4,4H_2O$ is heated at 800° in a current of hydrogen fluoride, or by igniting thorium silicofluoride in a current of hydrogen. The same powder is produced by the action of hydrofluoric acid on thoria. The anhydrous product is obtained by leading hydrogen fluoride over anhydrous thorium chloride or bromide heated to 350–400°.[1]

Potassium Thorofluoride, $K_2ThF_6,4H_2O$, is obtained by boiling the hydroxide with potassium fluoride and hydrofluoric acid, in the form of a heavy, black powder. When a solution of the chloride is precipitated with acid potassium fluoride the compound $K_2ThF_6,4ThF_4,H_2O$ is thrown down. Other double fluorides with potassium fluoride are known, but as they are all insoluble in water and hydrofluoric acid, it is uncertain whether they are definite compounds or mixtures.[2]

Thorium Chloride, $ThCl_4$.—This is obtained by heating the oxide mixed with carbon in a current of chlorine, by heating a mixture of the dioxide and phosphorus pentachloride in an evacuated tube, by heating the dioxide at a red heat in a current of carbon monoxide and chlorine, vapour of carbon tetrachloride, chlorine and sulphur monochloride, or phosgene. It has the specific gravity 4·59, melts at 820° (Moissan and Martinsen),[3] and sublimes in white, shining tablets, its vapour density being 12·42, corresponding to the above formula. It deliquesces on exposure to the air, and its solution may be obtained by dissolving the hydroxide in hydrochloric acid. The anhydrous chloride combines readily with ammonia to form a series of compounds with 4, 6, 7, 12, and 18 molecules of ammonia. These compounds are all formed by the direct action of either gaseous or liquid ammonia on the anhydrous chloride and on keeping lose ammonia and form the compound $ThCl_4,4NH_3$. This latter compound is stable up to 120°, at 250° it is converted into the *tetra-amide*,

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[1] Chauvenet, *Compt. rend.*, 1908, 146, 489.

[2] Rosenheim, Samter, and Davidsohn, *Zeit. anorg. Chem.*, 1903, 35, 424.

[3] *Compt. rend.*, 1905, 140, 1510.

$Th(NH_2)_4$, and at a red heat into the *di-imide*,[1] $Th(NH)_2$. The strongly concentrated solution solidifies to a fibrous, crystalline mass which on heating emits hydrogen chloride. It forms hydrates with 2, 4, 7, 8, and 9 molecules of water, whilst a number of oxy- and hydroxy-chlorides have been described.[2] It forms with the chlorides of the alkali metals easily soluble double salts, as $KCl,2ThCl_4,18H_2O$.

Thorium forms a bromide and an iodide which are similar in their behaviour to the chloride.

Thorium Sulphide, ThS_2.—The metal burns in sulphur vapour with great brilliancy, forming a yellow powder which exhibits a metallic lustre under the burnisher, and has probably the above composition (Berzelius). It has been prepared pure by passing dried hydrogen sulphide over thorium sulphate at a low red heat. It is a yellow powder which inflames spontaneously in the air.[3] When carbon disulphide vapour is passed over thorium dioxide heated to redness it yields the *oxysulphide*, ThOS, as a light brown substance.[4]

Thorium Sulphate, $Th(SO_4)_2$, is obtained by dissolving the oxide in hot concentrated sulphuric acid, or by rubbing up powdered thorite or orangite to a paste with sulphuric acid, and heating the mixture to 500° until all the excess of sulphuric acid is driven off. The mass is then treated with cold water and boiled; a crystalline precipitate remains, and this may be purified by repeated solution in cold water and reprecipitation by boiling. If the solution be allowed to evaporate at the ordinary temperature, transparent monoclinic crystals of $Th(SO_4)_2,9H_2O$ are deposited, whereas above 43° a hydrate with $4H_2O$ is formed. Other hydrates with 2, 6, and 8 molecules of water are known.[5] Thorium sulphate forms double salts with the sulphates of the alkali metals; $Th(SO_4)_2,2K_2SO_4,2H_2O$ crystallises in regular prisms, which are easily soluble in water but do not dissolve in a solution of potassium sulphate. Thorium sulphate forms a number of basic sulphates, and combines with pyridine, quinoline, phenylhydrazine, and diethylamine to form well crystallised derivatives.

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[1] Chauvenet, *Compt. rend.*, 1910, 151, 387; *Ann. Chim. Phys.*, 1911, [8], 23, 275.

[2] Rosenheim and Schilling, *Ber.*, 1900, 33, 977; Rosenheim, Samter, and Davidsohn, *Zeit. anorg. Chem.*, 1903, 35, 424; Krüss, *ibid.*, 1897, 14, 361.

[3] Hauser, *Zeit. anorg. Chem.*, 1907, 53, 74. Compare also Duboin, *Compt. rend.*, 1908, 146, 815.

[4] Krüss, *Zeit. anorg. Chem.*, 1894, 6, 49.

[5] Roozeboom, *Zeit. physikal. Chem.*, 1890, 5, 198.

Thorium and Nitrogen.—A nitride, Th_3N_4, is formed[1] when metallic thorium is heated in a current of nitrogen, and when the carbide is heated in ammonia or the di-imide in either ammonia or nitrogen,[2] whilst a nitride of the same composition is obtained by reducing the dioxide with magnesium or aluminium in an atmopshere of nitrogen.[3] The latter compound, however, differs from the former in that it is not decomposed by water.

Thorium Nitrate, $Th(NO_3)_4.12H_2O$, is a very soluble salt crystallising in large, deliquescent tablets. Nitrates have also been obtained crystallising with $6H_2O$ and $5H_2O$,[4] and many double salts with other nitrates are known.[5] Complex compounds with antipyrine, pyridine, quinoline, and diethylamine have also been prepared.

The *phosphate* is insoluble both in water and phosphoric acid.

Thorium Borides, ThB_4 and ThB_6, have been prepared by heating thorium dioxide with amorphous boron in the electric furnace.[6]

Thorium Carbide, ThC_2, is prepared by heating thoria with sugar charcoal in the electric furnace, and forms a crystalline mass which is only slightly affected by concentrated acids but readily dissolves in dilute acids and is decomposed by water with evolution of a mixture of methane, ethylene, acetylene, and hydrogen.[7]

Thorium Silicide, $ThSi_2$, is obtained by heating a mixture of the double fluoride of potassium and thorium, potassium silicofluoride, and powdered aluminium at 1200°, or by heating silicon with thoria in the electric furnace.[8] It forms tetragonal plates of specific gravity 7·96.

Thorium Carbonates.—No normal metacarbonate, $Th(CO_3)_2$, of thorium has been obtained, but the *ortho-carbonate*, $ThCO_4$, is known. This compound is obtained by treating thorium hydroxide with carbon dioxide under a pressure of 30–40 atmospheres. At ordinary pressures a basic carbonate, $Th(OH)_4CO_2$, is obtained. When ammonium carbonate solution is added to solutions of thorium salts precipitates of basic carbonates are obtained. These dissolve in excess of alkali carbonates and yield solutions from which crystalline double carbonates of the type $3Na_2CO_3Th(CO_3)_2,12H_2O$ may be separated. Thorium carbonate forms a double carbonate with thallium carbonate of the formula $Th(CO_3)_2,3Tl_2CO_3$.

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[1] Matignon and Delépine, *Compt. rend.*, 1901, **132**, 36.

[2] Chauvenet, *Ann. Chim. Phys.*, 1911, [8], **23**, 425.

[3] Kohlschütter, *Annalen*, 1901, **317**, 158. Compare Matignon and Delépine, *Ann. Chim. Phys.*, 1907, [8], **10**, 130.

[4] Fuhse, *Zeit. angew. Chem.*, 1897, **4**, 115.

[5] Meyer and Jacoby, *Zeit. anorg. Chem.*, 1901, **27**, 359.

[6] Binet du Jassonneix, *Compt. rend.*, 1905, **141**, 191.

[7] Moissan, *Compt. rend.*, 1896, **122**, 573; see also Moissan and Étard, *Ann. Chim. Phys.*, 1897, [7], **12**, 427.

[8] Hönigschmid, *Compt. rend.*, 1906, **142**, 280.

DETECTION AND ESTIMATION OF THORIUM.

388 The compounds of this metal give no characteristic blowpipe or flame reaction. The alkalis and ammonium sulphide precipitate from its solutions the hydroxide insoluble in excess, and the carbonates give rise to a precipitate of a basic carbonate, which dissolves in an excess of the reagent. Ammonia produces no precipitate in this solution as it does in the corresponding one containing zirconium. Another characteristic property of thorium is its reaction with potassium sulphate, and especially the fact that the thiosulphate is thrown down from thorium solutions on addition of potassium thiosulphate, a reaction by which this metal may be separated from the metals of the cerium group. In order to separate it from titanium, columbium, and tantalum, ammonium oxalate is added to the solution, when the thorium alone is precipitated; if, however, an excess of ammonium oxalate be used the thorium oxalate dissolves. Thorium can be separated from zirconium by throwing down both metals as oxalates by ammonium oxalate, and then adding an excess of oxalic acid, when the zirconium oxalate dissolves completely, leaving behind the oxalate of thorium. Thorium is estimated as the oxide, obtained by igniting the precipitated hydroxide.

The Atomic Weight of thorium was determined by several chemists without concordant results. Thus Berzelius[1] found 235·5, and Delafontaine[2] 229·7 as the mean of several well-agreeing analyses of the sulphate. Cleve, by the same method, obtained the number 232·6, whilst analyses of the oxalate yielded him the number 232·2. On the other hand, Krüss and Nilson, by analysing the carefully purified sulphate, obtained as a mean of several consistent experiments,[3] the number 232·4, which is now (1922) adopted.

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[1] *Pogg. Ann.*, 1829, **16**, 385.

[2] *Arch. Sci. phys. nat.*, 1863, **18**, 343.

[3] *Ber.*, 1887, **20**, 1665. Compare Meyer and Gumperz, *Ber.*, 1905, **38**, 819.

THE GERMANIUM GROUP.

GERMANIUM. Ge = 72·5. At. No. 32.

389 This element was discovered in 1886 by Winkler in the course of an investigation of a new silver mineral found at Freiberg in 1885, and termed argyrodite, $GeS_2,4Ag_2S$. The preliminary investigation led him to suppose that the new element would occupy the vacant place between antimony and bismuth in the periodic classification,[1] but further examination showed that the new element was tetravalent, and identical with the ekasilicon predicted by Mendeléev. The close agreement between the predicted properties of the element and its compounds and those actually observed by Winkler, has already been mentioned (p. 70).

Germanium is an extremely rare element: argyrodite and canfieldite,[2] a mineral of similar composition from Bolivia, contain 6–7 per cent. of the metal, but these are both rare. Traces of germanium have been found in several minerals, particularly in zinc blendes, the richest source of the element now known being retort residues from the smelting of zinc from certain localities. It is separated by a process depending on the volatility of the tetrachloride; 100 grams of the impure zinc oxide are dissolved in 200 c.c. of concentrated hydrochloric acid. On distillation in the presence of chlorine, or some other oxidising agent which prevents arsenic from volatilising, the distillate which passes over between 121° and 140° contains all the germanium.[3]

Metallic germanium is best obtained by the reduction of germanium dioxide with carbon at a full red heat. The semi-crystalline regulus is washed with water to remove carbon, and fused with a little borax. It is thus obtained as a greyish-white, brittle, lustrous metal, which frequently crystallises in octahedra,[4] has a specific gravity of 5·469, melts about 960°, and is not markedly volatile at 1350°. It oxidises at a high temperature, is insoluble in hydrochloric acid, but dissolves in aqua

[1] *Ber.*, 1886, 19, 210.

[2] Penfield, *Amer. J. Sci.*, 1893, [3], 46, 107.

[3] Buchanan, *J. Ind. Eng. Chem.*, 1917, 9, 661. See also Dennis and Papish, *J. Amer. Chem. Soc.*, 1921, 43, 2131.

[4] See Kolkmeijer, *Proc. K. Akad. Wetensch. Amsterdam*, 1922, 25, 125.

regia, and is converted by nitric acid into the dioxide. It combines directly with the halogens.

COMPOUNDS OF GERMANIUM.

390 Germanium forms two oxides, germanium dioxide, GeO_2, and germanium monoxide, GeO.

Germanium Dioxide, GeO_2, the most important of these, is obtained from argyrodite as follows: the powdered mineral, mixed with nitre and potassium carbonate, is introduced in small quantities at a time into a red-hot Hessian crucible. On cooling, two layers are obtained; the upper one, which contains all the germanium, is powdered, extracted with water, the solution treated with sulphuric acid, and evaporated to dryness. The acid residue dissolves in cold water, but almost all the germanium is deposited as oxide on standing; the remainder is precipitated as sulphide and converted into oxide by heating with nitric acid. To purify the crude oxide, it is dissolved in hydrofluoric acid, and potassium fluoride added; potassium fluogermanate separates out, and is converted into a soluble thio-salt by fusion with potassium carbonate and sulphur, this being decomposed by sulphuric acid, and the germanium precipitated as sulphide with sulphuretted hydrogen. The sulphide, mixed with a little sulphuric acid and heated, yields a mixture of sulphide and oxide, which is converted into the pure oxide by roasting and treating with nitric acid. Thus prepared, it forms a dense, white powder, somewhat soluble in water, 1 part of the dioxide dissolving in 247·1 parts of water at 20°, and in 95·3 parts at 100°; the solution on evaporation deposits microscopic rhombic crystals. Germanium dioxide has acid properties, but also dissolves in acids; it is readily reduced by carbon, sodium, and magnesium.

No germanium hydroxide of definite composition has been prepared, but a colloidal hydrate is obtained by decomposing an alkaline solution of the dioxide with carbon dioxide.

Germanous Oxide, GeO, is obtained by heating the dioxide with a small quantity of magnesium, or by heating the hydroxide; it forms a greyish-black powder. The corresponding *Hydroxide* $Ge(OH)_2$, is obtained as a yellow or yellowish-red precipitate by the action of alkalis on germanium dichloride or germanium chloroform, and is soluble in excess of the alkali. Hantzsch[1] has shown that when this excess is neutralised with hydrochloric acid, some germanous hydroxide remains in solution.

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[1] *Zeit. anorg. Chem.*, 1902, 30, 289.

From the conductivity of this solution and also of the alkaline solution, and from measurements of the rate at which the alkaline solution saponifies ethyl acetate, he concludes that germanous hydroxide in aqueous solution is a weak monobasic acid of the same type as formic acid, and has the constitution HGeO·OH, whilst in alkaline solution the salt HGeO·ONa is present. In aqueous solution part of the hydroxide is also present in the form $Ge(OH)_2$.

Germanium Hydride, GeH_4, is formed when the tetrachloride is reduced with sodium amalgam. The hydrogen evolved burns with a bluish-red flame which deposits a mirror on a cold porcelain surface. A mirror may also be obtained in the same way as in Marsh's arsenic test, and on heating in air is converted into the white dioxide. The hydrogen evolved as above gives a black precipitate with silver nitrate, and this on treatment with nitric acid gives germanium dioxide.[1]

Germanium Tetrafluoride, GeF_4, has not been prepared in the anhydrous state, but large crystals containing three molecules of water are obtained by concentrating a solution of the dioxide in hydrofluoric acid. It combines with hydrofluoric acid to form *fluogermanic acid*, which has not been prepared pure; its *potassium* salt, K_2GeF_6, is prepared by adding potassium fluoride to a solution of the dioxide in hydrofluoric acid, and forms hexagonal crystals, isomorphous with those of ammonium silicofluoride which are sparingly soluble in cold, but readily in hot water.

Germanium Tetrachloride, $GeCl_4$, is obtained by the direct union of germanium and chlorine, but is best prepared by heating the metal or the sulphide with mercuric chloride; it is a thin, colourless liquid, which fumes in the air, has a specific gravity of 1·887 at 18°, and boils at 86·5°.[2] It is slowly decomposed by water with formation of hydrated germanium dioxide.

Germanium Chloroform, $GeHCl_3$.—When germanium is heated in a current of hydrogen chloride it becomes red hot, and a distillate is obtained which, after exposure to the air, separates into two layers. The heavier of these consists of germanium chloroform, which is a colourless, fuming liquid, boiling at 75°. The lighter layer is *germanium oxychloride*, $GeOCl_2$, which is also a colourless liquid, but is less mobile than germanium chloroform, does not fume in the air, and boils considerably above 100°. *Germanium dichloride*, $GeCl_2$, is also known; it is a colourless, fuming liquid.

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[1] Voegelen, *Zeit. anorg. Chem.*, 1902, **30**, 325. See also Paneth, Matthies, and Schmidt-Hebbel, *Ber.*, 1922, **55**, [*B*], 775, 2615; Müller and Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 1909; Schenck, *Rec. trav. chim.*, 1922, **41**, 569.

[2] Dennis and Hance, *J. Amer. Chem. Soc.*, 1922, **44**, 299.

Germanium Disulphide, GeS_2.—This compound, which is the most characteristic of the germanium derivatives, is prepared by the action of sulphuretted hydrogen on a solution of germanium dioxide, or by the addition of an excess of a mineral acid to a solution of an alkali thiogermanate, sulphuretted hydrogen being passed through the solution to complete the precipitation. It is a white powder, only wetted with difficulty by water. It is appreciably soluble, 1 part dissolving in 221·9 parts of cold water; it also readily dissolves in ammonium sulphide. The thiogermanates are obtained by fusing germanium derivatives with an alkali carbonate and sulphur.[1]

Germanium Monosulphide, GeS, is obtained by carefully heating the disulphide in a current of hydrogen, and forms thin plates having a greyish-black colour and an almost metallic lustre. The reduction easily proceeds further, with formation of metallic germanium. When dissolved in alkalis and reprecipitated by acid, it forms brown flakes soluble in hot concentrated hydrochloric acid with evolution of hydrogen sulphide.[2]

DETECTION AND ESTIMATION OF GERMANIUM.

391 Germanium salts impart no colour to the Bunsen flame, but the spark spectrum exhibits a number of bright lines, especially in the blue and violet regions, the following among others having been measured: 6021, 5893, 5131, 4814, 4746, 4685, 4261, 4179. It is most readily recognised by the precipitation in strongly acid solution of a white sulphide, which is readily soluble in alkalis or ammonium sulphide, and slightly soluble in water: this compound is also the most suitable yet known for its gravimetric estimation. When an aqueous solution of hydrofluoric acid containing any germanium compound is saturated with solid potassium chloride, a grey, gelatinous precipitate of potassium fluogermanate is formed.

Atomic Weight of Germanium.—By the analysis of pure germanium chloride, Winkler, in 1886, found the atomic weight to be 72·5. More recently, Müller, by conversion of potassium fluogermanate to potassium chloride, has obtained the number 72·42.[3]

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[1] *J. pr. Chem.*, 1886, [2], 34, 162; 1887, [2], 36, 177.

[2] *Ber.*, 1888, 21, 131.

[3] *J. Amer. Chem. Soc.*, 1921, 43, 1085.

TIN (Stannum). Sn = 118·7. At. No. 50.

392 This metal was known in early times. It is very uncertain whether the word "bedil" in the Old Testament, which is translated by the Greek word *κασσίτερος*, and by the Latin *stannum*, was originally used to designate tin. It is likewise doubtful whether the metal which the Phœnicians are said to have brought from the Cassiterides, the exact locality of which was unknown to Herodotus, was really tin. Possibly the Greek word is connected with the Arabic "kasdir," which signifies tin. It is, however, certain that at the beginning of our era the word was used to specify tin, for Pliny states that *cassiteron* and *plumbum candidum* are the same, and he adds that it is more expensive than *plumbum nigrum* (lead); he moreover states that it serves for soldering the latter metal, and that it is obtained from the Cassiterides in the Atlantic Ocean. That the Cassiterides really were the British Islands appears more than probable, for after Cæsar's conquest tin was carried from the Cornish mines through Gaul, by way of Marseilles to Italy;[1] and Diodorus Siculus mentions that the inhabitants carry the tin to a certain island called Iktis, lying on the coast of Britain. "During low water the intermediate space is left dry, and they then carry over abundance of tin to this place in their carts." There can be little doubt that the Iktis of Diodorus is St. Michael's Mount, in Mount's Bay, in Cornwall; for up to the present day a causeway exists, flooded at high water, but dry at low water, across which the inhabitants are in the habit of carrying goods to and from the mainland. The names by which Pliny designates tin and lead seem, however, to show that he did not consider these as distinct metals, but rather as varieties of one metal, and he adds, "Sequitur naturæ plumbi cujus duo genera, nigrum atque candidum." The word *stannum*, which at a later period became the general designation for tin, also occurs in Pliny's works, though it appears certain that by this word he did not signify tin, but rather any mixture of metals which contains lead. In the works of the Latin Geber the most important properties of tin are mentioned, such as the peculiar crackling sound which the metal emits when bent, as well as the fact that it forms brittle alloys. Tin was termed Hermes by the early Greek alchemists, but about A.D. 500 it received the name of Zeus or Jupiter, and

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[1] G. Smith, *The Cassiterides.* London, 1863.

to it the sign ♃ was given; owing to the above-mentioned property of forming brittle alloys it was, however, sometimes termed *diabolus metallorum*.

Tin has been found in small quantities in Siberia, Guiana, and Bolivia in the native state, together with metallic gold, though the metallic tin from the last-named locality may, according to Forbes, possibly have been an artificial product. It has also been found in small tablets in bismuthite from Mexico.

The chief ore of tin is cassiterite, or tinstone, a more or les pure form of the dioxide, SnO_2. Less frequently it is found a tin pyrites, $Cu_4SnS_4,(Fe,Zn)_2SnS_4$, and occasionally as silicat It also occurs in small quantity in certain epidotes, as well as i columbites, tantalites, and other similar minerals. Various mineral waters contain traces of tin, and this metal has also been detected in certain meteoric masses.

393 *The Metallurgy of Tin.*[1]—Almost all commercial tin is obtained from tinstone, which is found in veins traversing the older crystalline and schistose rocks, and also as *stream tin* in water-worn nodules amongst the detritus of the same rocks. Tin ore is not, however, very widely distributed, only occurring in large quantities in a few localities. The oldest and best known tin mines from which tin has continuously been obtained, probably from the time of the Phœnicians up to the present, are those of Cornwall. The ore there occurs in the granite and in the metamorphic schistose rock, and is found especially rich in the killas, a metamorphic clay slate, and in the line of junction of this with granite. It is found in veins or lodes, in beds or flats, and in ramifications of small veins or "stock-werke," and these tin veins usually run in Cornwall in an easterly or westerly direction. The following minerals are frequently found together with tinstone: wolfram, apatite, topaz, mica, tourmaline, arsenical pyrites, etc.

Tin mines exist, though on a much smaller scale than in Cornwall, in other parts of Europe, as in Saxony, Bohemia, Russia, Sweden, France, and in the Spanish province of Galicia. Very large deposits of tin ores are, however, found in other quarters of the globe. The principal producers of tin ore are, at the present time, the Malay Peninsula, Bolivia, the Dutch Islands of Banca and Billiton, Australia and Tasmania, Yunnan in China, and Nigeria. All these produce more tin ore than

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[1] See also *Metallurgy of Tin*. Henry Louis. McGraw-Hill Book Company, 1911.

Cornwall. Tin has also been found in Mexico, South Africa, Japan, Siam and Burma.

Tin ores may be smelted in shaft furnaces or in reverberatory furnaces, but as the ores obtained are generally very poor, containing only from 1 to 2 per cent. of tin, preliminary operations of dressing or concentration are always necessary, and as considerable losses are experienced in these operations, much attention is being given to the direct treatment of tin-bearing material, and many suggestions have been put forward. These, however, are not in a sufficiently advanced state to be considered in detail.

The process adopted in Cornwall for the reduction of the metal is a simple one. The ore, after being stamped, is washed to free it as much as possible from gangue, and is then roasted in calcining furnaces for the purpose of driving off the sulphur and arsenic contained in the arsenical and ordinary pyrites, if these be present. The vapours from these revolving calcining furnaces are led into chambers in which the arsenious oxide condenses. The construction of an Oxland and Hocking's revolving calciner is shown in Fig. 183. This consists of a long cylinder lined with firebrick and placed in an inclined position. The fire (H) is placed at the lower end (A), whilst the upper end is in connection with chambers in which the arsenious oxide condenses. The ore is dried on the top of these chambers, which are made of iron plate, and then brought by means of the hopper (h) into the cylinder, the roasted ore falling down into the space (F). This then undergoes a second washing in order to remove the ferric oxide and other oxidised materials, and if copper or bismuth be present, is treated with dilute sulphuric or hydrochloric acid for its removal. After these operations the roasted ore is found to contain from 60 to 70 per cent. of tin. It sometimes happens that the tin ore is mixed with more or less wolfram, (Fe,Mn)WO_4, and as this mineral possesses a high specific gravity it cannot be removed from the tin ore by washing. In order to remove this impurity, the presence of which in the smelting operations would prove injurious to the quality of the tin obtained, the ore is passed through some form of magnetic separator which extracts the wolfram and allows the tinstone to pass on. The prepared tin ore, or *black tin*, is then mixed with one-fifth part its weight of anthracite and the mixture sprinkled with some water in order to prevent the finely divided ore from being blown by the draught into the flues. The construction of the reverberatory furnace is shown in Figs. 184 and 185; the charge is introduced

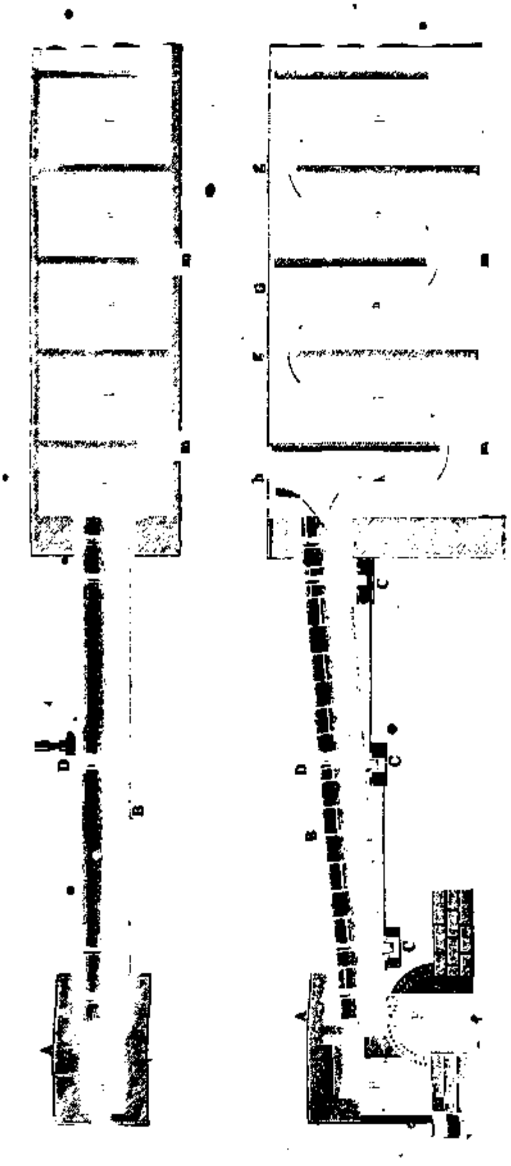

Fig. 183.

by the door (B) on to the hearth (A), and then worked through the door (E). The temperature of the furnace is gradually raised for five hours, the charge then repeatedly stirred, and at the

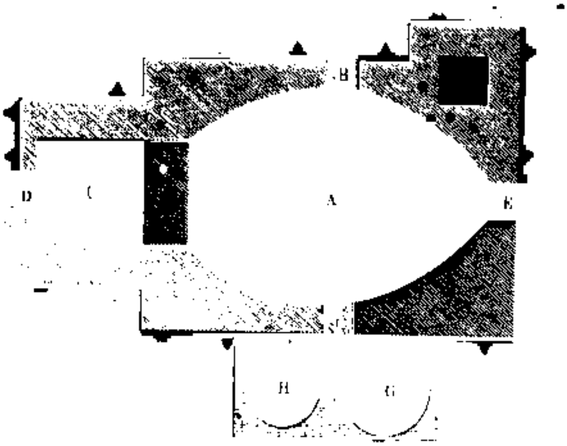

FIG. 184.

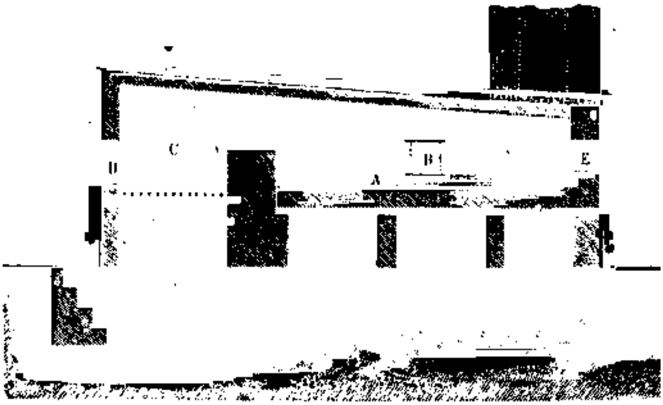

FIG. 185.

expiration of six hours the reduced metal is tapped and allowed to run from the lower part of the hearth through the hole (f) into the vessel (G). The impure tin thus obtained is then cast into moulds, and these are refined by the process of *liquation*. This is effected by placing the ingots in another similar reverberatory furnace which is gradually heated, so that the pure, more easily fusible tin first melts and runs into a cast-iron vessel (H) placed below, whilst the less fusible alloy of tin with iron and arsenic remains on the hearth. A fire is placed under the vessel (H) in order to keep the metal liquid, and this is then stirred up with a pole of green dense wood. The length of this operation depends upon the quality of the metal which it is desired to obtain, and may last from one to several hours. The dross which separates during the process of refining, and the "hard-head," or residue which remains on the hearth, both of which contain large quantities of tin, are afterwards worked up. In order to prepare *grain tin*, the tin is heated until the metal becomes brittle and crystalline; it is then broken up by a hammer, or allowed to fall from a considerable height.

The slags formed during the smelting operations generally contain sufficient tin to be worth extraction. This tin may exist as prills of metal or in chemical combination. The metallic portion is often separated by crushing and washing, or by allowing the slag to stand in a molten condition for some hours, when the metallic tin settles to the bottom. Slags containing tin in the combined condition are re-smelted with dross and other residues and strong bases at high temperatures in shaft or reverberatory furnaces.

394 *Separation of Tin from Tin Scrap, etc.*—Tin is separated from tin scrap and tin can waste by means of dry chlorine gas. The tin waste is washed in an alkaline bath to remove grease, rinsed in water, then heated in a furnace to remove solder, and then treated in iron cylinders with chlorine, the cylinders being kept cool.[1] The tin chloride thus formed is put on the market, and the steel scrap, which contains less than 0·1 per cent. tin, is hydraulically pressed into briquettes, and smelted in open-hearth furnaces.

The electrolytic process formerly used, in which sodium hydrate was the electrolyte, proved expensive, as it required highly paid labour, expensive electric current, and gave as a product a tin mud of inferior quality, which required further smelting treatment to convert it into marketable tin.

The total amount of tin produced in 1919 was about 113,893 tons.[2]

395 *Properties and Uses of Tin.*—Tin is a white, brightly

[1] *Ost. Zeit. f. Berg. u. Hutt-Wesen*, 1909, 57, 103.

[2] *Mineral Industry*, 1919, 28, 665.

lustrous metal, which melts at 232° (Heycock and Neville), boils under atmospheric pressure at about 2270° (Greenwood),[1] and has a specific gravity at 13° of 7·293 (Matthiessen). Its specific heat is 0·05363 at 0°, 0·05549 at 54°, and 0·05690 at 97·6° (Griffiths).[2] Its atomic heat is therefore 6·37—6·76. Its average compressibility between 100 and 500 megabars is 0·000,001,7 (Richards and Stull).[3] It is harder than lead, but softer than gold. It exhibits a fibrous fracture, and when bent emits a peculiar crackling sound caused by the friction of the crystalline particles. Tin can be easily rolled or hammered out to foil, and at a temperature of 100° it may be drawn into wire, which, however, possesses but slight tenacity; at 200° it becomes so brittle that it may be powdered. A sample of Banca tin which was exposed at St. Petersburg to a very low temperature during the winter of 1867–8, fell to granular, crystalline pieces or to a coarse powder. This alteration is due to the fact that tin, like sulphur, exists in more than one form, dependent upon the temperature, the stable form below 18° being the grey powder or "grey tin." At ordinary temperatures common white tin is in a metastable condition, but the change to the stable grey tin takes place with extreme slowness. The rate of change may, however, be accelerated by lowering the temperature, the maximum velocity being reached at −50°. This alteration was known to Aristotle, who speaks of tin as "melting" when kept at low temperatures.[4] Between 18° and 194° the stable form of tin is tetragonal, whilst above this temperature it is rhombic.[5] If zinc be brought into a solution of tin chloride the metal separates out in the form of fine crystalline dendrites, and this deposit, known as the tin-tree (Arbor Jovis), was first prepared by Ilsemann in 1786. When tin is melted and then allowed partially to solidify, the liquid portion being poured off, needle-shaped prismatic or tabular crystals of the metal remain behind. Another mode of obtaining crystalline tin is to decompose tin chloride by a weak electric current, when the metal is deposited in tetragonal prisms and pyramids. Fine crystals of tin can also be obtained when water containing zinc dust in suspension is gradually added to a solution of tin chloride.

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[1] *Proc. Roy. Soc.*, 1909, **82**, [*A*], 396.

[2] *Ibid.*, 1913, **88**, [*A*], 549.

[3] *Pub. Carn. Inst.*, **76**, 1907.

[4] Cohen and van Eyk, *Zeit. physikal. Chem.*, 1899, **30**, 601; Hasslinger, *Monatsh.*, 1908, **29**, 787; Cohen, *Zeit. physikal. Chem.*, 1908, **63**, 625; 1909, **68**, 214.

[5] Findlay, *The Phase Rule*, p. 39 (Longmans); Cohen and Goldschmidt, *Zeit. anorg. Chem.*, 1904, **50**, 225; Jänecke, *Zeit. physikal. Chem.*, 1915, **90**, 313.

Metallic tin remains bright in dry or moist air at the ordinary temperature, but when melted it gradually oxidises, forming a greyish-white skin on the surface, which consists of a mixture of tin and stannous oxide and is gradually oxidised to the dioxide. It is dissolved by dilute, and more rapidly by concentrated hydrochloric acid, with evolution of hydrogen and formation of stannous chloride; it dissolves also in aqua regia and in hot concentrated sulphuric acid, and is converted by somewhat diluted nitric acid into metastannic acid. It dissolves also in aqueous solutions of the alkalis, with formation of salts of metastannic acid and evolution of hydrogen.

Tin is used for a large number of purposes, for the preparation of vessels for household and technical use, for the manufacture of tinfoil, for tinning copper and iron, and especially for preparing the alloys of tin. Tinned copper vessels were employed by the ancients, for we find them described by Pliny; and the same author also mentions as a well-known fact that in the process of tinning, the weight of copper articles increases but slightly, and he adds that the substance termed stannum is employed for this purpose.

Copper- and brass-ware can readily be tinned by dipping the vessel into the molten metal. In order to cover the interior of a vessel with a coating of tin, it is heated and some molten tin poured in, which is then well divided over the surface by rubbing with rags. In order to prevent the oxidation of the metal, a small quantity of resin or sal-ammoniac is added. Agricola was the first to mention the process of tinning iron. It appears, however, that at that time it was only slightly employed. The process is usually supposed to have been discovered in Bohemia in 1620, coming into use in England and France about 100 years later. In the modern process of preparing the common tin plate, an important industry in South Wales, mild steel plates, after being annealed, rolled and "pickled" in weak acid solutions, are dipped in a bath of molten tin. On the surface of this is a layer of zinc chloride which acts as a flux, and the plates have to pass through this before they reach the tin. In the bath they pass under a partition and emerge through a layer of hot grease, which floats on the surface of the tin and is separated from the flux by the partition. The plates pass between rollers to remove the excess of tin, and are then polished.

Alloys of Tin.

396 Several of these alloys are largely employed in the arts. Tin and lead may be mixed in any proportion, and the alloys are harder and tougher, but more readily fusible than either of the two metals. For this reason they are employed as solders. The following table gives the composition of some of the different lead and tin alloys:

	Common Pewter.	Solder.		
		Fine.	Common.	Coarse.
Tin	4	2	1	1
Lead	1	1	1	2

In practice, a certain amount of antimony is often used to replace some of the tin in these alloys.[1]

Bronze is the name given to any alloy consisting chiefly of copper and tin, although other elements are frequently added to impart particular properties.

The alloys corresponding in composition to the formulæ $SnCu_3$ and $SnCu_4$ are definite chemical compounds, and are the only ones of the series which remain homogeneous after melting, a certain amount of liquation taking place in all the others. The hardness of these alloys increases as the proportion of copper is increased from pure tin to 35 per cent. of copper; from 35 per cent. to 73 per cent. of copper the alloys are extremely brittle, and beyond 73 per cent. of copper, the hardness diminishes as the copper is increased. The effect of heat on some of the copper-tin alloys is remarkable, for whilst steel is hardened by quenching in water, these alloys are hardened by slow cooling and when quenched in water they lose their brittleness and become malleable.

Gun-metal usually contains 9 parts of copper to 1 of tin, and has a yellow colour. This alloy also serves for the preparation of bronze medals.

Speculum-metal is composed of 1 part of tin to 2 parts of copper melted together, with, frequently, addition of a small quantity of arsenic. It possesses a steel-grey colour, is very brittle, and takes a very high polish.

Bell-metal possesses a varying composition. It generally consists of from 4 to 5 parts of copper to 1 of tin. It has a yellowish-grey colour, and readily melts to form a thin liquid. It has a finely granular structure, is hard, brittle, and very

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[1] See Bannister and Tabor, *Journ. Inst. Metals*, 1909, 2, 58.

ANALYSES OF ALLOYS OF TIN.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
Cu .	91·74	67	73·94	82	84·25	87·89	84·53	85·9	70·30	89·43	89·78	88·77	89·34	84·20
Sn .	8·26	33	21·67	17	15·64	10·58	6·82	14·1	24·53	8·17	9·16	9·25	7·50	3·05
Pb .	—	—	1·19	—	—	—	8·65	—	5·20	1·05	1·33	0·71	1·21	0·75
Fe .	—	—	0·17	1	trace	0·27	—	—	—	0·34	—	—	—	—
Zn .	—	—	—	—	—	—	—	—	—	—	0·35	1·28	1·61	11·55
Ni .	—	—	2·11	trace	—	—	—	—	—	0·19	—	—	—	—

I. English gun-metal.
II. Speculum metal used in construction of Lord Rosse's large telescope.
III. Bell cast in 1670 in Darmstadt.
IV. Chinese gong.
V. Egyptian bronze coin of the reign of Ptolemy IX.
VI. Attic bronze coin.
VII. Roman bronze coin of Justinian.
VIII. Gaulish axe.
IX. Celtic arrow-head.
X. Bronze statue of sixteenth century from Augsburg.
XI. Statue of Germanicus, cast in Berlin in 1824.
XII. Thorwaldsen's Shepherd, cast in Berlin in 1825.
XIII. Statue of Bacchus in Berlin, 1830.
XIV. Statue of Lessing in Brunswick.

sonorous. The Chinese gongs and tom-toms are cast at a very high temperature, and then quickly brought under the hammer; in consequence the alloy becomes very dense.

The preceding table gives the composition of some of the alloys described above.

Phosphor-bronze.—The addition of phosphorus to bronze imparts to it a character of greater hardness, elasticity, and toughness. This material is obtained by melting copper with tin phosphide, sometimes with a small addition of lead. It contains from 0·25 to 2·5 per cent. of phosphorus, and from 5 to 15 per cent. of tin, and is largely used, especially that containing from 7 to 8 per cent. of tin, for portions of machinery for which hardness and toughness are important properties. The alloy containing more tin has been employed for bell-metal. Its valuable properties are connected with the fact that copper forms a homogeneous alloy with tin phosphide, the presence of phosphorus preventing the oxides from dissolving and thus impairing the qualities of the metal.

Tin Amalgam.—Tin readily combines with mercury with lowering of temperature. The amalgam may be formed more quickly when mercury is poured into molten tin, and, according to the quantity of mercury added, the amalgam is either liquid, or forms a granular or crystalline mass. When mercury is made the negative pole in a solution of tin dichloride, fine crystals of the amalgam are obtained containing from 44 to 51 per cent. of tin (Joule). Tin amalgam was formerly largely used for silvering mirrors, but now has almost entirely been superseded by the use of silver.

It is not certain when tin amalgam was first employed for manufacturing mirrors, inasmuch as, during the middle ages, the processes used in the preparation of mirrors were kept secret. It is, however, clear that before amalgam was used, a surface of metallic lead was employed for obtaining a mirror as early as the thirteenth century, when such mirrors were common. These were curved, and were prepared, as Beckman described in his *History of Inventions*, from large glass globes, into the interior of which a mixture of resin, molten lead, and sulphide of antimony was introduced, the fluid mass being brought over the surface until it was all covered with a thin film. The globe was then cut into pieces, and the mirrors thus obtained were often employed as ornaments. A guild of glass-mirror makers existed at Nuremberg in the year 1373; whether they made mirrors according to the above process is doubtful, but they, as well as French workmen, sold products of their art in the Venetian market up to the year 1500. The use of amalgam for coating mirrors is first mentioned by Kunkel, who recommends for the purpose an amalgam of 2 parts of quicksilver, 1 part of marcasite (bismuth), ½ part of tin, and ½ part of lead.

COMPOUNDS OF TIN.

TIN AND OXYGEN.

397 The fact that tin readily forms a calx was observed at an early period. Pelletier was the first, in the year 1792, to show that tin combines in two proportions with oxygen, forming two series of salts. This investigation was continued by Proust, but for a long time considerable doubt existed as to the number of the oxidation products of the metal. Berzelius in 1812 assumed that there were three oxides, SnO, Sn_2O_3, and SnO_2, on the grounds that when the metal is oxidised by nitric acid the highest oxide thus prepared possesses a totally different chemical character from that obtained by precipitation with alkalis from a solution of the salts of tin. The subsequent investigations of Davy, Gay-Lussac, and Berzelius himself have proved that only the first and last of these oxides exist. A peroxide, SnO_3, has also been prepared.

Tin Monoxide or *Stannous Oxide,* SnO. This oxide may be prepared in a variety of ways. In the first place, it is obtained as an olive-coloured powder when stannous oxalate is ignited out of contact with air. Secondly, it may be prepared by adding a solution of potassium carbonate to one of tin dichloride, when a white precipitate having the composition $Sn_2O(OH)_2$ is thrown down. This readily absorbs oxygen from the air, but if it be washed in absence of air and dried in a stream of carbon dioxide, the monoxide remains behind as a black powder. Stannous oxide is also obtained when the pure dichloride is mixed with sodium carbonate, the mass heated until it has become black, and then lixiviated. If the hydrated oxide be boiled with a dilute solution of caustic potash, the anhydrous oxide is obtained as a crystalline powder, the crystals consisting of combinations of the cube and dodecahedron. It may also be obtained in the crystalline state by digesting a nearly saturated solution of the hydrated oxide in acetic acid at a temperature of 56°.

According to Hantzsch,[1] the hydroxide, SnO_2H_2, is precipitated when caustic soda is added to a solution of stannous chloride in the absence of air. It dissolves in excess of the reagent, and, like germanous hydroxide, acts as a weak monobasic acid, the solution containing sodium stannite, H·SnO·ONa.

Stannous oxide readily takes fire when heated in the air, and dissolves in acids with formation of stannous salts, to which it corresponds. These are, however, more readily obtained by the action of acids upon the metal, and possess an unpleasant metallic taste, redden litmus, owing to hydrolysis, readily absorb oxygen, and serve as powerful reducing agents.

Tin Dioxide or Stannic Oxide, SnO_2, occurs in nature as tinstone, or cassiterite, crystallising in the tetragonal system (Fig. 86), and possessing an adamantine lustre. The crystals are seldom colourless, being generally tinted brown or black from the presence of the oxides of manganese and iron. *Stream-tin* is found in water-worn nodules, and *Wood-tin* in reniform, fibrous masses. When tin is heated nearly to its boiling point in the air, it burns with a luminous, white flame, and the dioxide which is thus formed in a state of fine division was formerly known as *flores jovis*. If fused in the presence of air, the surface of the metal soon becomes covered with a grey pellicle, which then passes into a grey powder known as *flores stanni*, consisting of a mixture of finely-divided metal with the oxide; the mixture, on continued ignition, is wholly converted into stannic oxide. The dioxide is also obtained on treating tin with nitric acid, when a violent oxidation occurs. The hydrated white powder thus formed yields the dioxide on washing and igniting. If a solution of stannic chloride be precipitated with ammonia, a gelatinous precipitate is obtained which can be completely washed only with difficulty. If, however, it be heated with a concentrated solution of an alkali sulphate, a dense precipitate is thrown down, and this can be easily washed and yields the pure dioxide on ignition. An amorphous, white or straw-coloured powder is then obtained, which is quite insoluble in water and possesses a specific gravity of 6·71. On heating it changes colour, becoming lemon-yellow and then brown, but it assumes its original tint on cooling.

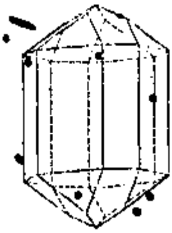

FIG. 186.

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[1] *Zeit. anorg. Chem.*, 1902, 30, 289; see also Bury and Partington, *Journ. Chem. Soc.*, 1922, 121, 1998.

The dioxide may also be obtained by the electrolysis of a solution of potassium or sodium chloride, a tin plate being used as anode, and one of platinum as cathode.[1]

By heating amorphous stannic oxide in a current of hydrogen chloride it may be obtained in microscopic crystals which have the form of cassiterite and a specific gravity of 6·72 (Deville).[2] The formation of crystalline stannic oxide has been observed in fusing the dross collected on the hearth of a gun-metal furnace, the crystals being hard, brittle, four-sided prisms.[3] Stannic oxide can be fused only at a very high temperature, according to Cusack[4] 1127°. It is not volatile, nor is it attacked by concentrated acids, with the exception of sulphuric acid.

Stannic Hydroxides.—Two stannic hydroxides are known, which have the same composition, H_2SnO_3, but different chemical properties. Berzelius,[5] who discovered the second form, introduced the term "isomerism" to designate this hitherto unknown phenomenon. They are both weak acids, but react differently with other acids, and form different salts with alkalis, from which they can be precipitated unchanged by the addition of acids: they are distinguished by the names *stannic* and *metastannic* or *α*- and *β-stannic acids.*

Berzelius showed that they are both in the same stage of oxidation. The difference is not due to their water content, for this is variable, depending on how they are dried, and the difference between the two forms persists through the varying degrees of hydration. Two views have been held as to the cause of the difference. The older is that the *β*-form is a polymer of *α*-stannic acid: the method of preparation of the *α*-acid, and the composition of its salts, make it probable that the molecule contains only one atom of tin, and that it has the simple formula H_2SnO_3: the work of Frémy[6] and Engel[7] on the salts and oxychlorides derived from *β*-stannic acid indicate that its molecule contains five atoms of tin, and that it can be given the formula $H_2Sn_5O_{11},4H_2O$. On the other hand, Mecklenburg[8] has produced evidence that the two forms are both colloidal hydrates, differing only in the size of their particles; while no clear line of demarcation can be drawn between the two forms, the *α*-acid consists of the relatively small particles and the β-acid of the larger ones.

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[1] Lorenz, *Zeit. anorg. Chem.*, 1896, **12**, 436.

[2] *Compt. rend.*, 1861, **53**, 161.

[3] Abel, *Journ. Chem. Soc.*, 1856, 119.

[4] *Proc. Royal Irish Acad.*, 1897, **4**, 399.

[5] *Annalen*, 1817, [2], **5**, 149.

[6] *Ann. Chim. Phys.*, 1848, [3], **23**, 385.

[7] *Compt. rend.*, 1897, **124**, 765; 1897, **125**, 464, 651, 709.

[8] *Zeit. anorg. Chem.*, 1909, **64**, 368; 1912, **74**, 207; 1914, **84**, 121. See also Collins and Wood, *Journ. Chem. Soc.*, 1922, **121**, 441.

Berzelius, Engel, and others have described a third form, *parastannic acid*. This is not an isomer of the α- and β-forms, since it has a different water content from either of the others when dried under similar conditions. It has the composition $H_2Sn_5O_{11},2H_2O$, and is obviously related closely to metastannic acid, and has been regarded as an internal anhydride of it; according to Kleinschmidt,[1] however, it is identical with it.

Stannic acid or α-stannic acid is obtained as a white, hydrated precipitate by the action of calcium carbonate or alkali on a solution of a stannic salt, or by the action of an acid on a stannate. Its water-content depends on how it has been dried; rapidly dried by suction and pressure it has the composition $SnO_2,4H_2O$ or $H_2[Sn(OH)_6]$; dried slowly in the air at room temperature, it has the composition $SnO_2,2H_2O$ or H_4SnO_4; dried in a vacuum over sulphuric acid it has the composition SnO_2,H_2O or H_2SnO_3, but it is doubtful if these are definite hydrates. The final product on heating is anhydrous stannic oxide. The freshly precipitated hydroxide, while still moist, dissolves slightly in water, to which it imparts an acid reaction, and is readily soluble in dilute acids, forming stannic salts, and in alkalis to form stannates. It is partially transformed to the β-form on drying or on standing in contact with water, especially on heating.

The Stannates.—Only one orthostannate, cobalt orthostannate, Co_2SnO_4, has as yet been prepared. It has been obtained by Hedvall[2] by fusing cobaltous and stannic oxides with potassium chloride and dissolving out the excess stannic oxide with hydrochloric acid.

The stannates of the other metals, when formed by fusion, have the formula $M^{I}_2SnO_3$, but when formed from solution have the formula $M^{I}_2SnO_3,3H_2O$. Bellucci and Parravano[3] argue that these are derivatives of hexahydroxy-stannic acid, $H_2[Sn(OH)_6]$; the three molecules of water are water of constitution, not water of crystallisation, since they are often not expelled by long heating at 100°. All the stannates examined, namely, those of sodium, potassium, lead, silver, calcium, strontium, and barium, contain three molecules of water; the potassium salt is isomorphous with the potassium salts of hexahydroxy-plumbic acid, $H_2[Pb(OH)_6]$, and the far more stable hexahydroxy-platinic acid, $H_2[Pt(OH)_6]$;

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[1] *Monatsh.*, 1918, 39, 149.

[2] *Arkiv Kem. Min. Geol.*, 1914, 5, No. 18, 1.

[3] *Zeit. anorg. Chem.*, 1905, 45, 142.

they are analogous to the hexachlorostannates, $H_2[SnCl_6]$, and an intermediate acid, $H_2[Cl_3Sn(OH)_3]$, exists.

The alkali stannates alone are soluble in water, and can be obtained as measurable crystals; stannates of the other metals are obtained as insoluble precipitates by double decomposition.

Potassium Stannate, K_2SnO_3, is obtained by fusing the dioxide with potash, or by dissolving the hydrated oxide in potash-lye. The solution yields on evaporation over sulphuric acid colourless, glistening, rhombic prisms of $K_2[Sn(OH)_6]$, which have an alkaline taste and are readily soluble in water. Metallic copper brought into contact with the solution becomes covered with a bright coating of tin.

Sodium Stannate, Na_2SnO_3, is prepared on a large scale and employed extensively in calico-printing under the name of *preparing salts*. It is obtained either by fusing the finely powdered or levigated tinstone with caustic soda, dissolving the mass in water to remove any ore that may be unacted upon, and evaporating the solution; or by heating tin with caustic soda and Chili saltpetre. On evaporating the solution, crystals of $Na_2SnO_3,3H_2O$, or $Na_2[Sn(OH)_6]$, are obtained, which are more soluble in cold than in hot water. A tolerably concentrated solution of the salt which contains no caustic soda deposits on cooling fine prisms of the composition $Na_2SnO_3,10H_2O$, and these effloresce on exposure to air.

Metastannic Acid and the Metastannates.—In his *Reflections on the Hypothesis of Alkali and Acidum*,[1] published in 1670, Boyle remarks that aqua-fortis eats up or destroys more tin than it dissolves. On the other hand, he elsewhere[2] mentions that a solution of tin in aqua-fortis readily becomes gelatinous. Kunkel, who also studied the action of nitric acid on tin, mentions in his *Laboratorium Chymicum* that tin can only be dissolved when it is added in small quantities to an acid, and that heat must be altogether avoided, because white calx of tin is thrown down when the acid is hot. The explanation of these different statements is to be found in the facts that when the metal is treated with weak nitric acid it forms either stannous or stannic nitrate, according to the degree of concentration of the acid, and that the latter salt easily decomposes with separation of a gelatinous stannic acid, whilst, on the other hand, when tin is acted upon by strong nitric acid it is violently attacked with evolution of heat and formation of an insoluble white powder consisting of a mixture of α- and β-stannic acids; Kleinschmidt, however, maintains that it is β-stannyl nitrate, $Sn_5O_9(NO_3)_2,4H_2O$, and that this is readily hydrolysed to β-stannic acid by washing with water. Metastannic acid is also prepared by the addition of acids to metastannates, or by their hydrolysis in dilute solution, by the hydrolysis of β-stannyl chloride, by the spontaneous change of α-stannic acid, and by the slow spontaneous hydrolysis of stannic salts and stannates. Engel finds that it has the composition $SnO_2,2H_2O$ or $H_2Sn_5O_{11},9H_2O$ when it is dried in the air, and SnO_2,H_2O or $H_2Sn_5O_{11},4H_2O$ when it is dried in a vacuum over sulphuric acid. According to van Bemmelen,[1] however, it always contains less water than the α-form when the two forms are treated similarly, and no definite hydrate exists. The final product on heating is stannic oxide.

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[1] Boyle, *Op.* 4, 284.

[2] "Experiments and Considerations Concerning Colours."

The freshly precipitated hydroxide reddens litmus paper, and is distinguished from α-stannic acid, inasmuch as it is altogether insoluble in nitric acid, and swells up but does not dissolve in strong sulphuric acid, forming the easily hydrolysed compound β-stannyl sulphate, $Sn_5O_9SO_4 \cdot 4H_2O$ (Kleinschmidt). Hydrochloric acid produces a compound, meta- or β-stannyl chloride, which is soluble in water but insoluble in hydrochloric acid, and which Engel found to have the formula $Sn_5O_9Cl_2,4H_2O$. Numerous similar hydrated oxychlorides have been described.

Metastannates are produced by the action of alkalis on metastannic acid or on solutions of its chloride: the best known is sodium metastannate, which is slightly soluble in water but insoluble in excess of alkali. Frémy and Kleinschmidt find it can be represented by the formula $Na_2Sn_5O_{11},4H_2O$. Other metastannates of greater complexity have been described.

It is doubtful if any of these derivatives of the stannic hydroxides, except the easily crystallisable stannic salts and the stannates, are real compounds; their composition depends to a large extent on the method of preparation, and they are all readily hydrolysable. Mecklenburg has shown that the reaction between β-stannic acid and phosphoric acid is a typical adsorption effect. The composition of the product varies with the concentration of the phosphoric acid in the solution according to the usual law that holds when true chemical combination does not occur, but an adsorbed layer is formed on the surface of any very finely divided substance. It is probable that all the metastannates, metastannyl chlorides, and other compounds with acids are adsorption phenomena. Solutions of metastannyl chloride are not true solutions, but colloidal.

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[1] *Ber.*, 1880, 13, 1466.

Parastannic acid was discovered by Berzelius, who called it β-stannic acid; since then this name has been applied to metastannic acid. It has been studied by Engel, and is formed when metastannic acid is heated in water at 100°. Its reactions are almost identical with those of β-stannic acid, but it contains two less molecules of water in its composition:

	Dried in air.	Dried in a vacuum.	Potassium salt.	Chloride.
Metastannic acid .	$H_2Sn_5O_{11},9H_2O$	$H_2Sn_5O_{11},4H_2O$	$K_2Sn_5O_{11},4H_2O$	$Sn_5O_9Cl_2,4H_2O$
Parastannic acid .	$H_2Sn_5O_{11},7H_2O$	$H_2Sn_5O_{11},2H_2O$	$K_2Sn_5O_{11},2$ or $3H_2O$	$Sn_5O_9Cl_2,2H_2O$

Colloidal or *Soluble Stannic Acid* was obtained by Graham[1] by the dialysis of a mixture of tin tetrachloride and alkali, or of sodium stannate and hydrochloric acid, the gelatinous mass which is first formed gradually dissolving. The liquid is converted on heating into colloidal metastannic acid. Traces of hydrochloric acid or of a salt bring about gelatinisation in both solutions.

Tin Peroxide, SnO_3.—This oxide is known only in the hydrated condition, and is prepared by the addition of barium peroxide to a solution of stannous chloride containing hydrochloric acid. The barium chloride is removed by dialysis, and the colloidal solution is evaporated. A white mass having the formula $H_2Sn_2O_7$ or $2SnO_3,H_2O$ remains behind.[2]

When stannic hydroxide is heated with hydrogen peroxide at 70°, and the mixture is desiccated, a *perstannic acid*, $HSnO_4,2H_2O$, is obtained, and this on heating at 100° yields the acid $H_2Sn_2O_7,3H_2O$. Potassium and sodium stannates when similarly treated form salts corresponding to these acids.[3]

When concentrated alkali stannate solutions are electrolysed at low temperatures and with low current densities, perstannates are formed, owing to anodic oxidation.[4]

STANNOUS COMPOUNDS.

398 *Tin Difluoride* or *Stannous Fluoride*, SnF_2, is obtained by dissolving the hydrated monoxide in hydrofluoric acid. On evaporation in absence of air this compound is obtained in the form of small, white, monoclinic tablets.

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[1] *Phil. Trans.*, 1861, 151, 213.

[2] Spring, *Bull. Soc. chim.*, 1889, [3], 1, 180.

[3] Tanatar, *Ber.*, 1905, 38, 1184.

[4] Coppadoro, *Gazz.*, 1906, 36, i, 469.

Tin Dichloride or *Stannous Chloride*, $SnCl_2$, is obtained on the large scale by dissolving tin in hydrochloric acid. On evaporating the solution and cooling, crystals of hydrated stannous chloride, $SnCl_2,2H_2O$, known in commerce as *Tin Salt*, separate out in transparent, monoclinic prisms which melt in their water of crystallisation at 40°, and on cooling again yield a crystalline mass. They have a specific gravity of 2·71, and dissolve at the ordinary temperature in 0·37 part of water. When more strongly heated they partially decompose with evolution of hydrogen chloride, but when dried in a vacuum over sulphuric acid they lose their water. The anhydrous salt, which may also be obtained by heating tin in hydrogen chloride, or with the requisite amount of corrosive sublimate, is a transparent mass having a fatty lustre and conchoidal fracture. It fuses at 250° to form an oily liquid which boils at 606°. Its vapour at low temperatures has a density always less than that required by the formula Sn_2Cl_4, but at a high temperature the value becomes constant, agreeing with $SnCl_2$,[1] whilst the freezing point of urethane is lowered by dissolving stannous chloride in it by an amount corresponding to the formula $SnCl_2$.[2] The hydrated salt dissolves in a small quantity of water with lowering of temperature, forming a clear liquid which, when diluted with much water, becomes turbid, a basic chloride, $2Sn(OH)Cl,H_2O$, being precipitated; this again dissolves on the addition of acids. The same precipitate is formed when the clear solution is exposed to the action of the air:

$$6SnCl_2 + 2H_2O + O_2 = 2SnCl_4 + 4Sn(OH)Cl.$$

Stannous chloride is soluble in alcohol and in ether.[3] It combines with ammonia to form compounds which vary in composition according to the temperature of reaction.[4] When cooled in a freezing mixture, a yellow compound, $SnCl_2,2NH_3$, is formed, which blackens on exposure to light, and is decomposed by moisture into stannous oxide and ammonium chloride. At ordinary temperatures, a mixture of $SnCl_2,2NH_3$ and $SnCl_2,NH_3$ results, whilst at 100° $SnCl_2,NH_3$ only is formed. At 120—300°, the compound $3SnCl_2,2NH_3$ is formed as a brownish-red, crystalline mass, which is the most stable of the three compounds.

Tin Dibromide or *Stannous Bromide*, $SnBr_2$, is obtained when tin is heated in hydrogen bromide or distilled with mercuric bromide. It forms a light yellow, translucent mass fusing at 215·5°, and is soluble in water. A solution of this compound is obtained by acting with hot aqueous hydrobromic acid upon metallic tin.

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[1] Biltz and V. Meyer, *Ber.*, 1888, 21, 22.

[2] Castoro, *Gazz.*, 1898, 28, ii, 317.

[3] de Jong, *Zeit. anorg. Chem.*, 1902, 41, 596.

[4] Sofianopoulos, *Compt. rend.*, 1911, 152, 865.

Tin Di-iodide or *Stannous Iodide*, SnI_2, is best obtained by adding a small excess of iodide of potassium to a warm concentrated solution of stannous chloride. It crystallises in yellowish-red needles which dissolve only slightly in water, though readily in warm solutions of the chlorides and iodides of the alkali metals, and also in dilute hydrochloric acid. It melts at 316° solidifying to a crystalline mass which liquefies at a higher temperature. When heated in absence of air it is obtained in the form of a red, crystalline mass, yielding a scarlet powder. On treatment with dry ammonia, a yellow compound having the formula $SnI_2,2NH_3$ is formed.[1] If a saturated solution of stannous iodide in hydriodic acid be cooled to 0°, pale yellow needles of *iodostannic acid*, $HSnI_3$, are deposited. These are very unstable and readily decompose, forming stannous iodide.[2]

The fluoride, chloride, bromide, and iodide combine with the corresponding halide compounds of the alkali metals and with those of the metals of the alkaline earths to form crystalline double salts.

Tin Monosulphide or *Stannous Sulphide*, SnS, is obtained by heating together the metal and sulphur. Thin tin foil takes fire spontaneously when brought into sulphur vapour. When thus obtained, it is a lead-grey, tough, crystalline mass, which melts at a higher temperature than the metal. When a solution of stannous chloride is saturated with sulphuretted hydrogen, a brown hydrated precipitate is obtained, which on drying becomes black. This is scarcely soluble in ammonium sulphide, but dissolves on the addition of sulphur, and is also soluble in the polysulphides of the alkali metals, the stannous sulphide being first converted by the sulphur into stannic sulphide, which then dissolves, forming ammonium thiostannate. When the dried precipitate is added to fused stannous chloride and the melted mass treated on cooling with dilute hydrochloric acid, stannous sulphide is obtained in metallic, glistening, crystalline scales, having a specific gravity of 4·973. The crystalline variety may also be obtained by heating the amorphous sulphide in the

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[1] Ephraim and Schmidt, *Ber.*, 1909, **42**, 3856.

[2] Young, *J. Amer. Chem. Soc.*, 1897, **19**, 851.

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electric furnace.[1] Amorphous tin sulphide dissolves readily in hot hydrochloric acid, whilst the crystallised substance dissolves less readily.

Stannous Sulphate, $SnSO_4$, is formed by dissolving the metal or the hydrated oxide in dilute sulphuric acid. On evaporation in a vacuum, microscopic, granular crystals are obtained which are only a little more soluble in hot than in cold water. The solution readily deposits a basic salt.

Stannous Nitrate, $Sn(NO_3)_2$.—This salt is obtained by the action of very dilute nitric acid on the metal, ammonium nitrate being simultaneously produced:

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

STANNIC COMPOUNDS.

399 *Tin Hydride.*—If an alloy of tin and magnesium, the composition of which corresponds to the formula Mg_2Sn, is dissolved in hydrochloric acid, the hydrogen evolved contains small amounts of a volatile hydride of tin. This is condensed by liquid air, and can be re-evaporated without decomposition. On passing through a heated tube, it is decomposed, with the formation of a characteristic tin mirror.[2]

Tin Tetrafluoride or *Stannic Fluoride*, SnF_4, is obtained as a hygroscopic, white, crystalline substance by the action of anhydrous hydrofluoric acid on stannic chloride.[3] It boils at 705°, subliming below this temperature, and has the specific gravity 4·78 at 19°. An aqueous solution of the fluoride may be obtained by dissolving the hydrated dioxide in hydrofluoric acid; the solution coagulates on boiling, and decomposes on evaporation with evolution of hydrogen fluoride. Gaseous ammonia combines with tin tetrafluoride at 43°, forming a white compound, SnF_4,NH_3, which loses very little ammonia even at 400°.[4] When the fluoride and ammonia are heated together in a sealed tube at 120—130°, $SnF_4,2NH_3$ is formed. Both these compounds are soluble in ammonia.

Liquid hydrogen sulphide decomposes the fluoride in a sealed tube, thus: $SnF_4 + 2H_2S = SnS_2 + 4HF$.

Chlorine compounds of phosphorus bring about an exchange of chlorine and fluorine, and metals react violently with the fluoride, liberating tin.

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[1] Mourlot, *Compt. rend.*, 1897, 124, 768.

[2] Paneth and Furth, *Ber.*, 1919, 52, [*B*], 2020. See also Paneth and others, *Ber.*, 1922, 55, [*B*], 760, 775.

[3] Ruff and Plato, *Ber.*, 1904, 37, 673.

[4] Wolter, *Chem. Zeit.*, 1912, 36, 165.

It combines with other fluorides, forming a characteristic series of double salts, the *stannifluorides*, which mostly crystallise well and are isomorphous with the corresponding double fluorides of silicon, titanium, germanium, and zirconium.[1]

Potassium Stannifluoride, K_2SnF_6,H_2O, is obtained by neutralising hydrofluoric acid with potassium stannate, or by treating stannic chloride with a cold solution of potassium fluoride.[2]

It crystallises in thin, nacreous tablets or in rhombic pyramids which are much more soluble in hot than in cold water. When the solution contains an excess of hydrofluoric acid, the salt K_2SnF_6,HKF_2 is deposited in monoclinic prisms.

The stannifluorides of sodium, ammonium, calcium, and magnesium are also crystalline soluble salts.

Tin Tetrachloride or *Stannic Chloride*, $SnCl_4$, was first mentioned by Libavius in 1605, who obtained it by distilling tin or its amalgam with excess of corrosive sublimate. It was termed by him *Spiritus argenti vivi sublimati*, but afterwards it received the name *Spiritus fumans Libavii*. For its preparation, the process originally proposed by Libavius may be employed, or chlorine may be passed over tin foil, tin-plate scrap (p. 877), or fused tin placed in a retort. When the stream of chlorine is quick, and especially if the gas-delivery tube dips into the molten metal, an evolution of light and heat is observed. It may also be prepared by passing chloroform vapour over the heated dioxide.[3]

Tin tetrachloride is a colourless, thin, fuming liquid, which solidifies at − 33°, has a specific gravity of 2·234 at 15°, and boils at 113·9°,[4] forming a colourless vapour having the normal specific gravity of 9·1997 (Dumas). At the boiling point it dissolves hombic sulphur, yellow phosphorus, and iodine, and can be mixed in all proportions with bromine and carbon disulphide. When mixed with turpentine so much heat is evolved that the hydrocarbon takes fire. Its property of fuming in the air depends on the fact that it absorbs atmospheric moisture. In 1770, Demachy observed that it solidified when brought into con-act with one-third of its weight of water to form a crystalline mass termed *butter of tin*. Several distinct hydrates soluble in water may be produced, according to the quantity of water which is added. Thus the compound $SnCl_4,3H_2O$ is formed by exposing the anhydrous chloride to the action of moist air, or by the evaporation of its aqueous solution. This hydrate crystallises in monoclinic needles which melt at 80°, and on cooling again solidify to a crystalline mass. A second hydrate, having the composition $SnCl_4,5H_2O$, is obtained by the addition of a sufficient quantity of water to the anhydrous chloride, or by the gentle evaporation of the aqueous solution. It is deposited in opaque, acute, monoclinic prisms, which melt at a low temperature and again solidify to a crystalline mass. Lastly, large transparent, monoclinic crystals of the hydrate $SnCl_4,8H_2O$ are deposited in the cold from a dilute solution. On boiling a dilute aqueous solution of tin tetrachloride, stannic hydroxide is formed; in very dilute solutions this precipitate forms on standing.

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[1] Marignac, *Ann. des Mines*, 1859, [5], 15, 221.

[2] Emich, *Monatsh.*, 1904, 25, 907.

[3] Renz, *Ber.*, 1906, 39, 249.

[4] Thorpe, *Journ. Chem. Soc.*, 1880, 37, 331.

Tin tetrachloride is employed by dyers as a valuable mordant. Drebbel in Holland is said to have made the discovery that by help of this salt a permanent red dye can be obtained from cochineal. Dyers were formerly in the habit of preparing this mordant, known by the old names of tin-composition, physic, or dyer's spirits, by dissolving tin, together with sal-ammoniac or common salt, in nitric acid, or by dissolving tin in aqua regia, whence the solution was formerly termed nitro-muriate of tin. It is usual now for dyers to employ the crystalline pentahydrate, $SnCl_4,5H_2O$, which is a commercial product known as *oxymuriate of tin*. It is also largely employed for weighting silk.

Anhydrous stannic chloride combines with ammonia to form a solid mass having the composition $SnCl_4(NH_3)_4$, which can be sublimed and is soluble in water without decomposition.[1] It can be obtained in crystals by evaporating the aqueous solution over sulphuric acid, but if it be allowed to stand for some days, or if the liquid be warmed, stannic hydroxide separates out in a gelatinous form. Tin tetrachloride combines also with many other chlorides to form crystalline compounds,[2] such as $SnCl_4,2SCl_4$. This is obtained by the action of chlorine on tin disulphide, and forms large, yellow crystals, which melt at a summer temperature, and decompose above 40°, with evolution of chlorine. If dry nitrous fumes are led into a solution of stannic chloride, the compound $SnCl_4,N_2O_3$ is deposited as a yellow, amorphous mass, and if this be sublimed or if the dry vapours from aqua regia be passed into the chloride, the compound $SnCl_4,2NOCl$ is produced, which crystallises in bright, shining octahedra. If a solution of stannic chloride in chloroform be used, a white precipitate of $SnOCl_2,3SnCl_4,N_2O_5$ is obtained, and this on heating yields a white sublimate of $SnCl_4,4NOCl$.[1] Stannic chloride also combines with phosphorus pentachloride to form the compound $SnCl_4,PCl_5$, which sublimes in glistening, colourless crystals, but when kept even in closed vessels falls to an amorphous powder. It has a peculiar, extremely pungent smell, and fumes strongly in the air. The compound $SnCl_4,POCl_3$ forms crystals which melt at 58°, and can be distilled at 180° without decomposition. This compound fumes strongly in the air, and is at once decomposed by contact with water.[2]

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[1] Persoz, *Ann. Chim. Phys.*, 1830, **44**, 322.

[2] H. Rose, *Pogg. Ann.*, 1837, **42**, 517.

Like the fluoride, stannic chloride readily yields a series of double salts known as the *stannichlorides*, which present a similarity to the platinichlorides, but are less stable than the latter salts.[3] The free acid, H_2SnCl_6, is obtained in thin plates containing $6H_2O$ by saturating the pentahydrate, $SnCl_4,5H_2O$, with hydrochloric acid gas at 28° and cooling to 0°.[4]

Ammonium Stannichloride, $(NH_4)_2SnCl_6$, separates as a crystalline powder when solutions of the two salts are mixed, and crystallises from dilute solution in small, regular octahedra. It dissolves at the ordinary temperature in 3 parts of water. Its concentrated solution can be boiled without decomposition, but when diluted tin hydroxide separates out. It was formerly much used by calico-printers under the name of *pink salt*, from its power of acting as a mordant for madder-red colours, but its use has been almost entirely superseded by the crystalline pentahydrated stannic chloride.

Tin Tetrabromide or *Stannic Bromide*, $SnBr_4$.—Tin and bromine unite together with evolution of light and heat. The bromide is best prepared by adding bromine very slowly to strips of tin, the temperature being kept between 35° and 59°.[5] It is a white, crystalline mass, which fumes strongly on exposure to air and is easily soluble in water. It melts at 33° and boils at

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[1] Thomas, *Compt. rend.*, 1896, **122**, 32.

[2] Casselmann, *Annalen*, 1852, **83**, 257.

[3] von Biron, *J. Russ. Phys. Chem. Soc.*, 1904, **31**, 489; Bellucci and Parravano, *Atti R. Accad. Lincei*, 1904, [4], **13**, ii, 307; von Biron, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 993, 994, 1036.

[4] Engel, *Compt. rend.*, 1886, **103**, 213; Seubert, *Ber.*, 1887, **20**, 793.

[5] Lorenz, *Zeit. anorg. Chem.*, 1895, **9**, 365.

201°. The specific gravity of the liquid is 3·349 at 35°, and its vapour density is 7·92.[1] It is easily soluble in cold water, forming a colourless liquid from which the hydroxide is deposited slowly at the ordinary temperature and quickly on boiling. It yields crystalline *stannibromides* with the alkali bromides.

Tin Tetraiodide, SnI_4.—When tin and iodine are heated together, combination commences at 50°, and at a higher temperature heat and light are emitted. In order to prepare this compound, tin filings are first moistened with carbon disulphide, and then iodine is gradually added. It crystallises in red octahedra, melting at 146° and having a specific gravity of 4·696. Tin tetraiodide boils at 295°, but sublimes at as low a temperature as 180° in yellowish-red needles, very similar in form to those of ammonium chloride. It is soluble in carbon disulphide, absolute alcohol, ether, chloroform, or benzene; with water it forms hydriodic acid and stannic oxide.

If ammonia be led into a solution of tin tetraiodide in carbon disulphide, and at the same time the solvent be allowed to evaporate, a white substance, $SnI_4,8NH_3$, is formed. This is also formed by passing ammonia over the tetraiodide.[2]

Tin Disulphide or *Stannic Sulphide*, SnS_2.—This compound, crystallising in six-sided tablets or in gold-coloured, translucent scales having a specific gravity of 4·425, is used as a bronze powder for the purpose of bronzing articles of gypsum, wood, etc., and is known in commerce as mosaic gold. The discovery of this compound is usually ascribed to Kunkel. He does indeed speak of a sublimation of sulphide of tin and sal-ammoniac, but expresses himself so vaguely that it is impossible to recognise this compound from his description. It was well known in the eighteenth century under the names of *mosaic gold*, *aurum mosaicum*, or *musivum*. It was then prepared as at the present day by subliming a mixture of tin amalgam, sulphur, and ammonium chloride, and as it was supposed to contain mercury it was often employed as a mercurial medicine. Peter Woulfe in 1771 showed that it did not contain mercury, and described other methods for its production, according to which it is still prepared. Thus, for instance, it is obtained in the form of a fine pigment by heating 18 parts of tin amalgam, containing 6 parts of mercury, with 6 parts of ammonium chloride and 7 parts of sulphur, when ammonium chloride, mercuric chloride, and stannous chloride sublime, and stannic sulphide remains behind in the form of golden-yellow scales. It is likewise prepared by heating tin monosulphide with 8 parts of mercuric chloride, or subliming tin filings with ammonium chloride and sulphur, and according to several other receipts given by Woulfe.[1] Pelletier believed mosaic gold to be a compound of sulphur with the highest oxidation product of tin, and Proust, who found that it could be obtained by heating stannous chloride or tin monoxide with sulphur, supposed it to be a compound of tin, sulphur, and a small quantity of oxygen. The exact composition was ascertained by J. Davy and Berzelius in the year 1812. The formation of mosaic gold from tin, sulphur, and ammonium chloride appears to take place according to the following equations (Gmelin):

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[1] Carnelley and O'Shea, *Journ. Chem. Soc.*, 1878, **33**, 55.

[2] Ephraim and Schmidt, *Ber.*, 1909, **42**, 3856.

$$\text{(I.)}\ Sn + 4NH_4Cl = (NH_4Cl)_2SnCl_2 + H_2 + 2NH_3$$
$$\text{(II.)}\ 2(NH_4Cl)_2SnCl_2 + S_2 = SnS_2 + 2NH_4Cl + (NH_4Cl)_2SnCl_4.$$

When heated, a portion sublimes without decomposition, but the greater part is resolved into sulphur and monosulphide. It is not attacked by hydrochloric or nitric acid, but readily dissolves in aqua regia, as well as in caustic potash, when potassium stannate and potassium thiostannate are formed. If sulphuretted hydrogen be led into a solution of the tetrachloride a yellow precipitate is obtained. This consists of a mixture of tin disulphide and tin dioxide, and is readily soluble in the sulphides of the alkali metals, when the *thiostannates* are formed.

Thiostannic Acid.—When dilute hydrochloric acid is added to a solution of thiostannate, a yellow precipitate is obtained, which on drying forms an almost black powder possessing a brown streak and wax-like lustre, and having the composition H_2SnS_3. When heated in absence of air it yields the golden-yellow disulphide.[2]

Potassium Thiostannate, $K_2SnS_3,3H_2O$, is prepared by boiling a concentrated solution of potassium sulphide with the necessary quantities of sulphur and tin; it crystallises in colourless prisms. By a similar process, the *sodium salt*, $Na_2SnS_3,2H_2O$, is obtained in yellow, vitreous, regular octahedra.[3] When sodium sulphide is fused with tin monosulphide and sulphur, a black, crystalline mass is obtained, yielding a dark-coloured solution, which on concentration at a low temperature yields colourless crystals resembling gypsum, and having the formula $Na_4SnS_4,12H_2O$.

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[1] *Phil. Trans.*, 1771, 61, 114.

[2] Kühn, *Annalen*, 1852, 84, 110.

[3] Ditte, *Compt. rend.*, 1882, 95, 641.

Ammonium thiostannate is formed by dissolving the sulphides in yellow ammonium sulphide, and may be precipitated by alcohol in unstable yellow tablets of the composition[1] $(NH_4)_2SnS_3,3H_2O$.

When mosaic gold is fused with iodine in absence of air, a crystalline mass of SnS_2I_4 is obtained, and this can be sublimed, or recrystallised from solution in carbon disulphide. It is decomposed by water into stannic oxide, sulphur, and hydriodic acid.

Stannic Oxysulphide, $Sn_2OS_3,11H_2O$.—This compound is obtained by allowing precipitated stannic sulphide to remain in contact with ammonia, filtering and acidifying the filtrate, or by digesting the sulphide with ammonium carbonate and acidifying the filtered solution. It is a white mass which is soluble in ammonia and gradually becomes yellow on keeping.[2]

Stannic Sulphate, $Sn(SO_4)_2$.—As already mentioned, tin dioxide dissolves in concentrated sulphuric acid, and from the solution two crystalline bodies may be obtained having the empirical formulæ $SnO_2,2H_2SO_4$ and SnO_2,H_2SO_4, which may be regarded as the normal sulphate, $Sn(SO_4)_2,2H_2O$, and the basic sulphate, $Sn(SO_4)_2,SnO_2,2H_2O$. Both of these are decomposed by water with separation of stannic oxide.

On mixing solutions of stannic acid in sulphuric acid, and calcium sulphate in sulphuric acid, and concentrating, regularly formed, colourless cubes are obtained of $Sn(SO_4)_2,CaSO_4,3H_2O$; similar salts are obtained with barium, strontium, and lead sulphates.[3]

Stannic Nitrate, $Sn(NO_3)_4$, is obtained as a white powder by the action of 70 per cent. nitric acid on tin, but must be quickly removed, as it is rapidly converted into the hydrated dioxide. It is a white substance which is stable in presence of concentrated nitric acid at 90°, but is immediately decomposed at 100°.[4] It dissolves in water, but the solution is almost immediately decomposed with separation of hydrated stannic oxide.

Potassium Ammono-stannate, $K_2[Sn(NH_2)_6]$, is produced by the action of potassamide on stannic iodide in liquid ammonia,[5] a reaction entirely analogous to the production of stannates by the action of alkalis in aqueous solution:

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[1] Staněk, *Zeit. anorg. Chem.*, 1898, **17**, 117.

[2] Schmidt, *Ber.*, 1894, **27**, 2739. See also *Chem. Centr.*, 1907, i., 397.

[3] Weinland and Kühl, *Ber.*, 1906, **39**, 2951. See also *Zeit. anorg. Chem.*, 1907, **54**, 250.

[4] Montemartini, *Gazz.*, 1892, **22**, 384.

[5] Fitzgerald, *J. Amer. Chem. Soc.*, 1907, **29**, 1693.

$$6KNH_2 + SnI_4 = K_2[Sn(NH_2)_6] + 4KI.$$
$$6KOH + SnI_4 = K_2[Sn(OH)_6] + 4KI.$$

If this is heated at 145°, it loses three molecules of ammonia, which is analogous to the behaviour of potassium stannate trihydrate:

$$K_2[Sn(NH_2)_6] = K_2Sn(NH)_3 + 3NH_3.$$
$$K_2[Sn(OH)_6] = K_2SnO_3 \quad + 3H_2O.$$

No more ammonia can be driven off by heating for several hours at 316°.

Tin and Phosphorus.—When finely-divided tin is heated in the vapour of phosphorus, a silver-white, very brittle mass, having the composition SnP, is obtained. This has a specific gravity of 6·56, and dissolves readily in hydrochloric acid, but is not attacked by nitric acid. When phosphorus is thrown on to the surface of molten tin, combination also takes place. The compound containing the largest quantity of phosphorus which can thus be obtained has a silver-white colour, is not very brittle, and may be cut with a knife; it appears to possess the composition Sn_3P_2 (Pelletier).[1] If spongy tin, obtained by precipitating a tin salt with zinc, be brought into contact with such a quantity of phosphorus that one atom of the latter be present to nine atoms of the metal, a phosphide having the composition Sn_9P is obtained. The same compound is formed whenever any of the other phosphides containing more phosphorus is heated. This is a coarse, crystalline mass, which has the appearance of cast zinc. It melts at 370°, and is used for the preparation of phosphor-bronze.

Stannic Pyrophosphate is obtained by the action of phosphoric acid on stannic acid, and is insoluble in water and in nitric acid. This reaction is employed for the separation of phosphoric acid from other bodies. For this purpose a known quantity of tin foil is added to the nitric acid solution of the body under investigation, when the whole of the phosphoric acid remains behind with the metastannic acid.

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[1] See also Stead, *J. Soc. Chem. Ind.*, 1897, **16**, 200, 309; and Jolibois, *Compt. rend.*, 1909, **148**, 636.

DETECTION AND ESTIMATION OF TIN.

400 When a small quantity of a tin compound is held in the reducing flame on charcoal, a malleable bead of metal is obtained, which easily dissolves in hot hydrochloric acid. This solution gives with a small quantity of mercuric chloride a white precipitate which becomes grey on boiling:

$$\text{(I.) } SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$$

$$\text{(II.) } SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2Hg.$$

If one of the metallic globules be fused in a borax bead slightly tinted with cupric oxide and heated in the reducing flame, the bead will become of a red tint, due to the formation of cuprous oxide.

Stannous salts yield a brown precipitate of stannous sulphide with sulphuretted hydrogen, which dissolves in ammonium sulphide containing polysulphides; the solution, on addition of an acid, deposits stannic sulphide. Ammonia and caustic alkalis give a white precipitate of stannous hydroxide, which is soluble in excess of the latter reagents. Stannous chloride gives a blue coloration with ammonium molybdate, and in this way 1 part of tin as stannous chloride may be detected in 1,500,000 parts of solution.[1]

Stannic salts yield a yellow precipitate of stannic sulphide with sulphuretted hydrogen, readily soluble in ammonium sulphide, and alkalis precipitate stannic hydroxide, which dissolves in an excess of the precipitant.

Zinc precipitates metallic tin from solutions of the tin salts in the form of glistening scales, or in a spongy or arborescent mass. The tin salts do not impart any colour to the non-luminous gas-flame, but the spark spectrum of the chloride exhibits two characteristic lines having wave-lengths of 4526 and 5631 (Lecoq de Boisbaudran). These same lines are seen together with others in the spark spectrum of the metal, the most brilliant of the tin lines being as follows (Thalén): 6452, 5798, 5631, 5588, 5563, 4526.

In the processes of qualitative analysis tin is obtained together with those metals which are precipitated by sulphuretted hydrogen in an acid solution. To separate tin from these the well-washed precipitate is treated with yellow ammonium sulphide, filtered, and the filtrate acidified with cold dilute hydrochloric acid. The precipitate may contain, beside stannic sulphide, the sulphides of arsenic and antimony. After it has been well washed with water, it is digested with solid ammonium carbonate to dissolve the sulphide of arsenic. The residue is then dissolved in concentrated boiling hydrochloric acid, the solution boiled with metallic copper, and the liquid tested for stannous chloride with mercuric chloride (see also under Antimony).

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[1] Longstaff, *Chem. News*, 1899, 80. 282; Rogers, *J. Amer. Chem. Soc.* [illegible] 23. 220.

Tin may be estimated as the oxide. If the metal or one of its alloys be under examination, it is oxidised with pure, tolerably strong nitric acid, and the well-washed residue ignited. From solution it is precipitated with ammonia as the hydroxide, but if it be present in the form of stannous salt it must be first oxidised with chlorine or hydrochloric acid and potassium chlorate. The precipitate obtained by ammonia is then dissolved in the smallest quantity of hydrochloric acid and heated with a concentrated solution of sodium sulphate, when the hydroxide is again precipitated, and this is not gelatinous, and may therefore be easily washed (Löwenthal). When tin sulphide is obtained in the separation of tin from the other metals, it can be gradually converted into stannic oxide by gentle roasting and subsequent ignition.

Tin is frequently estimated by volumetric methods, the processes depending on the oxidation of stannous chloride to stannic chloride by means of standard solutions of ferric chloride or iodine.

The electrolytic method has been employed for estimating tin as the metal, the process being carried out in the presence of ammonium oxalate or some other organic salt.[1] It may be deposited also from solutions in ammonium sulphide.

Atomic Weight of Tin.—The early determinations of the atomic weight of tin were made by oxidising the metal to the dioxide, but the numbers obtained varied considerably. Thus Berzelius[2] found the number 117·65, and Mulder and Vlaanderen[3] 116·3, whilst a later determination by the last named gave the higher value 118·16. Dumas[4] by the same method obtained the number 118·06. Bongartz and Classen[5] employed four different methods, namely, the oxidation of pure tin with nitric acid, and the electrolysis of potassium stannichloride, ammonium stannichloride, and stannic bromide. The average of the most trustworthy experiments gave the number 119·0. *Briscoe*,[1] *by analysis of the tetrachloride*, obtained the number 118·7, which is now (1922) adopted.[2] This number has been confirmed by Baxter and Starkweather,[3] by electrolysis of stannic chloride, and by Krepelka,[4] by analysis of the tetrabromide.

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[1] Engels, *Ber.*, 1895, **28**, 3162; Hollard, *Compt. rend.*, 1897, **124**, 1451; Fischer, *Ber.*, 1903, **36**, 2348; etc.

[2] *Pogg. Ann.*, 1826, **8**, 177.

[3] *J. pr. Chem.*, 1849, **49**, 35.

[4] *Ann. Chem. Pharm.*, 1860, **113**, 26.

[5] *Ber.*, 1888, **21**, 2900.

LEAD. (Plumbum) Pb = 207·20. At. No. 82.

401 The first mention of lead occurs in the well-known passage in the Book of Job, Chap. XIX, and it is mentioned also in the Book of Numbers, Chap. XXXI, as a portion of the spoil taken from the Midianites. It is found under the name of óphéret, derived from the word áphár, signifying to have a grey appearance. In the oldest Greek translations of the Old Testament the word *μόλιβος* occurs, and this as well as the word *μόλυβδος* undoubtedly refers to lead. It appears that no exact distinction was drawn between the metals lead and tin during the time of the Israelites, but we find that Pliny points out a distinction between these two metals, inasmuch as he gives the name of *plumbum nigrum* to lead, whilst tin is designated as *plumbum candidum* (p. 872). Lead was known to the ancient Egyptians, as lead plates have been found in the Temple of Rameses III.

It has already been stated that the seven metals known to the ancients were supposed to be in some way connected with the seven heavenly bodies which were then known to belong to our solar system. Dull, heavy lead was apportioned to Saturn, and this metal is designated in the writings of the alchemists by the sign ♄.

Lead is seldom found in the free state in nature. Native lead does, however, occur in small quantities in certain lead ores, and in volcanic tufa. The oxides of lead are found in the form of rare minerals, the yellow oxide, PbO, and the red oxide or red lead, Pb_3O_4. The commonest ore of lead is galena or lead sulphide, PbS; this is very widely distributed, generally occurring together with quartz, calc-spar, fluor-spar, and heavy-spar, in the older as well as in the more recent strata, and in almost every part of the world. Thus in Cornwall it occurs in veins in the coarse argillaceous schist, provincially termed killas; in Derbyshire, Cumberland, Northumberland, and Yorkshire, it is found in mountain limestone; in Cardiganshire and Montgomeryshire it occurs in the Lower Silurian; and the chief deposits in the United States likewise occur in the same formation. Again, at Sala in Sweden, it is found in granular limestone, and in Freiberg in a schistose gneiss, older than the carboniferous system. Enormous quantities of galena, closely associated with zinc blende, occur in the Broken Hill deposits of Australia, in Burma, Rhodesia, etc. Sulphide of lead also occurs in combination with the sulphides of antimony and copper in the minerals zinckenite, $PbSb_2S_4$, and bournonite, $CuPbSbS_3$. In addition to these ores, lead carbonate occurs as the mineral cerussite, $PbCO_3$, found in some localities, as in the neighbourhood of Aix-la-Chapelle and of Santander in Spain, in sufficient quantity to be worked. It is also found in the lead mines of Cornwall and Devonshire, in Yorkshire, at Leadhills in Scotland, and at Seven Churches in County Wicklow. Other naturally occurring compounds of lead are the basic chloride, occurring as the minerals matlockite, Pb_2Cl_2O, and mendipite, $Pb_3Cl_2O_2$, and the sulphate of lead or anglesite, $PbSO_4$, found associated with galena and carbonate of lead at Leadhills and in other localities. Again, we have a basic sulphate called lanarkite, $PbO,PbSO_4$; leadhillite, $PbSO_4,3PbCO_3$; phosgenite, $PbCl_2,PbCO_3$; stolzite or lead tungstate, $PbWO_4$; wulfenite or lead molybdate, $PbMoO_4$; crocoisite or lead chromate, $PbCrO_4$; pyromorphite or lead phosphato-chloride, $3Pb_3P_2O_8,PbCl_2$; mimetesite or lead chloro-arsenate, $3Pb_3As_2O_8,PbCl_2$; as well as compounds of lead with the rarer elements, such as selenium, tellurium, selenic acid, vanadic acid, etc.

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[1] *Journ. Chem. Soc.*, 1915, **107**, 63.

[2] Aston, *Nature*, 1922, **109**, 813, has shown that there are eight isotopes of tin of atomic weights, 120, 118, 116, 124, 119, 117, 122, 121.

[3] *J. Amer. Chem. Soc.*, 1920, **42**, 905.

[4] *Ibid.*, 925.

By far the greater quantity of the total lead brought into the markets of the world is derived from galena.

402 *Smelting of Lead.*—Lead is an easily reducible metal requiring but simple processes for its production, and it was produced in England during the Roman occupation in a variety of localities. Numerous pigs of Roman lead have been found bearing Latin inscriptions. Whether lead was reduced in England before this period appears doubtful; the remains of rude furnaces in which lead ore was smelted in early times are, however, found in Derbyshire and elsewhere, and are termed *boles* by the inhabitants. In these furnaces, the heat

was not urged by an artificial blast of air, but piles of stone were built on the western brow of some eminence so as to employ the natural currents of air on mountainous places. A mixture of ore and charcoal was introduced into the interior of these furnaces, the lead being run out at the bottom after the operation.

The form of furnace next employed was the *ore-hearth*, a small, rectangular blast-furnace blown by bellows worked by means of a water wheel.[1] Modifications of this furnace are still in use in certain localities.

About the middle of the eighteenth century lead smelting in reverberatory furnaces appears to have been introduced into England from Flintshire, where it was in use in the year 1698.

Three distinct processes are employed for lead smelting. The first of these, known as the *air reduction process* (Percy), is employed when the ore consists mainly of galena, and is free from silica and the sulphides of other metals. The second, or *carbon reduction process*, is employed for less pure ores and consists in the roasting of the ore and the subsequent reduction of the lead oxide by carbonaceous matter. The third process is known as the *precipitation process*, the reduction of the lead being effected by metallic iron; this is chiefly practised in France, Germany, Spain, and North America, where the ore contains other metals, such as copper, antimony, and arsenic. It is however, to be remembered that two or even three of the above processes are often worked in the same furnace with the same charge of ore.

In the *air reduction process* the galena is roasted in a reverberatory furnace until a portion of the sulphide is converted into oxide and sulphate; the temperature is then raised, when metallic lead is formed together with sulphur dioxide. The following reactions are usually given as representing the interaction of the unaltered lead sulphide with the oxide and sulphate:

$$2PbO + PbS = 3Pb + SO_2.$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

In presence of an excess of sulphur dioxide, however, lead is partially reconverted into sulphide and sulphate:[2]

$$2Pb + 2SO_2 = PbS + PbSO_4.$$

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[1] See H. L. Pattinson, "Description of Lead-Smelting in the North of England." *Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-on-Tyne*, vol. 2, part i.; also J. J. Brown, jun., "Lead Smelting in the Ore-Hearth," *Trans. Am. Inst. Min. Eng.*, 1911, 42, 402.

[2] Jenkins and Smith, *Proc. Chem. Soc.*, 1897, 13, 104; Schenck and Rassbach, *Ber.*, 1907, 40, 2185, 2947.

The reverberatory furnaces used for the English process of lead smelting are of two kinds, the Flintshire furnace and the flowing furnace. The difference between these is that in the first the slag is raked out in pasty lumps, whereas in the flowing furnace the slag is tapped out in the molten state and termed run-slag. The reaction which takes place during the early stages of reduction is identical in both cases, but, in the flowing furnace, metallic iron is added to assist in the reduction of sulphide of lead.

Fig. 187 shows the construction of the Flintshire furnace. The usual charge of ore is 20 cwt. This is introduced by means of a hopper (T) in the arch of the furnace. The hearth of the furnace (B) is hollowed out as shown in the figure to permit the lead to flow through a tapping hole into an iron pot placed in front of the furnace. The charge is evenly spread over the surface and gently heated, the ore being well rabbled at intervals, and the temperature carefully regulated by opening or closing the various doors, so as to maintain the mass as hot as is possible without causing it to clot together; a portion of the sulphide is oxidised to oxide and sulphate, and the mass thus prepared for the following stage of the operation. During this part of the process the skimmings from the lead run off from the previous operation, which consist chiefly of lead containing a little sulphide, are added, and are quickly acted on by the lead oxide and sulphate with formation of metallic lead, which is run off from the tap-hole and contains more silver than the subsequent portions of the metal. After about two hours the temperature is raised to a bright red heat, the metal being formed in quantity, whilst

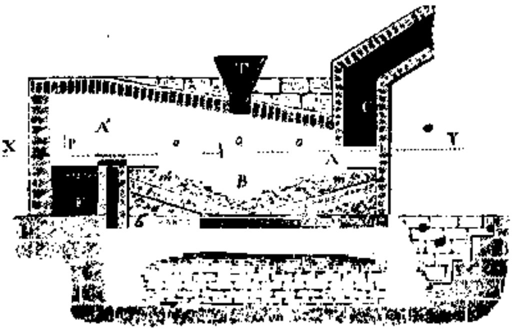

FIG. 187.

from time to time, in addition to stirring the mass, a small quantity of lime is added to stiffen the unreduced portion. This part of the process extends over an hour, and then for three-quarters of an hour the temperature is further raised and an additional small quantity of lime added, which besides lessening the fusibility of the mass also liberates any lead oxide which may have combined with the silica, and allows it to be reduced by the lead sulphide. Finally, the furnace is raised for three-quarters of an hour to the highest attainable temperature and a sufficient quantity of lime added partially to solidify the slag, which is raked out, and the lead run off from the tap-hole in the usual manner.

The *grey slag* obtained may contain as much as 40 per cent. of lead, and is further worked up in the slag-hearth, which is a small shaft furnace, or may be mixed in with the charge for the larger blast furnaces.

Reduction of Lead in Blast Furnaces.—This is the method now most generally adopted, as it is suitable for any class of ore and the percentage of lead may be much lower than that necessary for the other methods, whilst the presence of silica to a certain extent is not disadvantageous. For ores such as those which occur in the Harz, where the galena is mixed with iron and copper pyrites, zinc blende, fahl-ore, bournonite, and zinckenite, the blast furnace method gives the best results, and this is suitable also for the reduction of the oxides or carbonates of lead. The process for sulphide ores consists first in roasting to get rid of sulphur and then smelting the roasted ore with fluxes and reducing agents in the blast furnace. The roasting was formerly effected in heaps, in shaft furnaces or reverberatory furnaces, the latter being worked by hand or mechanically.

Several new methods of roasting galena have been introduced, in which the ore is mixed with lime, gypsum, oxide of iron or other material, damped and fed on to a small fire in a converter-shaped vessel, through which air is blown,[1] or fed on to some type of sintering machine such as is used in the various Dwight-Lloyd[2] processes for down-draft roasting. The chief advantage of these processes lies in the fact that the product obtained is very suitable for blast-furnace treatment, but besides this the cost is less, the losses of metal are less, and the production of fine material is greatly reduced.

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[1] *Mineral Industry*, 1905, **14**, 402; see also "Lead-Smelting and Refining," by W. R. Ingalls, published by the *Engineering and Mining Journal*, 1906; for "The Theory of Blast Roasting of Galena," see Bannister, *Trans. Inst. Min. and Met.*, 1912, **21**, 346.

[2] *Report of Seventh Internat. Cong. App. Chem.*, 1909, III, *A*, 20.

The blast furnace mostly used for lead and silver-lead smelting is rectangular in plan, about 44 inches wide and 144 inches long inside at the tuyere level. Fig. 188 is a section of such a furnace, which comprises a crucible portion (A), a shaft (B), extending from the crucible to the feed-floor (C), and a stack from

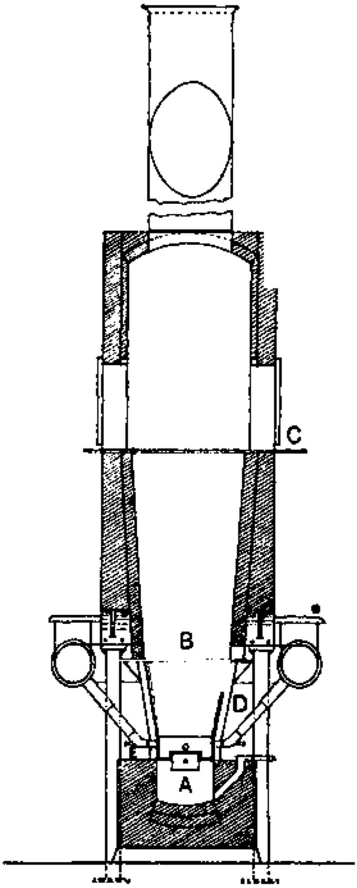

Fig. 188.

the feed-floor upwards. The furnaces are water-jacketed about the lower portion or bosh of the shaft, these jackets being made of cast iron or of steel, and through them water circulates continually. These jackets are shown at D, and through the side jackets the tuyeres (E) pass into the furnace. The shaft above these jackets is lined with firebrick, although in the newer furnaces the water jackets are carried to the top.

An Arents syphon tap is often fitted to the crucible portion of these furnaces for continuously drawing off the lead. When the ores contain copper the roasting is not carried so far, a certain amount of sulphur being left in the ore to combine with the copper for the formation of a cupriferous matte, and in this case a certain amount of unaltered lead sulphide will always be present in the matte. The furnace charge consists of a mixture of roasted ore, carbonaceous fuel, generally coke or a mixture of coke and charcoal, old slags and fluxes. The fluxes most used are ferruginous ores, often carrying silver or gold, which is collected partly in the lead and partly in the matte if this be also formed, ferruginous slags containing an excess of ferrous oxide, and sometimes lime or limestone. The slag should contain between 30 and 35 per cent. of ferrous oxide, between 10 and 30 per cent. of lime, and between 30 and 50 per cent. of silica. The lead present in the form of oxide is reduced partly by the carbon monoxide in the gases and partly by solid carbon; that present as sulphide, by iron, generally formed by reduction of the oxide of iron present in the charge. Any silicate present is reduced by the action of carbon in the presence of ferrous oxide or lime, and any lead sulphate present is reduced by reaction with sulphide, or is converted into sulphide by the action of carbon and this sulphide reduced by metallic iron.

Softening of Lead.—The lead produced in these processes is hard, owing to the presence of small quantities of antimony, arsenic, copper, zinc, iron, tin, bismuth, and sulphur, and it is necessary to remove these in order to render the lead marketable. Silver is also generally present and is removed by special processes, which are described later, and which enable the silver to be recovered. It is also necessary to remove impurities before desilverisation, as copper, antimony and arsenic interfere with the Pattinson process, and these, together with nickel and cobalt, interfere with Parkes's process.

For the purpose of removing the impurities, the lead is melted in a reverberatory furnace at a low temperature. Copper forms an alloy with some of the lead which is less fusible than lead itself and this separates out as a scum on the molten lead and may be removed; all the other commonly occurring impurities except bismuth are more readily oxidised than lead and are oxidised in the furnace together with a portion of the lead, the mixed oxides forming a dross on the surface which is removed from time to time. Bismuth cannot be got rid of in this manner, but it is concentrated with the silver in the Pattinson process for desilverisation. The hearths of modern reverberatory furnaces for the softening of hard lead consist of wrought iron pans lined with two thicknesses of firebrick and are often water-jacketed at the sides to diminish the corrosive action of the oxides formed on the material composing the hearth.

Condensation of Lead Fume.—During the smelting processes a large amount of lead fume is carried away in suspension in the waste gases from the furnaces, and many devices have been introduced for condensing and collecting these fumes, for subsequent treatment. In many works the arrangement consists merely in having very long flues between the furnaces and the chimney, the amount of condensation depending on the length of the flue. In other works more complete condensation is effected by arrangements for lowering the velocity of the gases, by first passing the exit gases through large chambers containing baffle plates, and then through iron flues cooled by the air. Other methods for condensing the fume consist of using a water spray or causing the gases to pass through layers of water on their way to the chimney. "Bag houses" are largely used for the condensation of lead fume; in the use of these, the cooled gases are forced through canvas or twill bags on their way to the chimney. Electrostatic methods of precipitating the fume have been introduced into some works.

403 *Desilverisation.*—Ordinary lead obtained by any of the above-mentioned processes always contains silver, and a very considerable proportion of the silver which now comes into the market is obtained from argentiferous galena. In former times the only process by which this silver could be extracted was cupellation, by which the whole of the lead is oxidised, whilst metallic silver remains behind. The oxide has then to be again reduced to metallic lead. It is, however, generally admitted that the process of cupellation cannot be economically carried on in the case of lead which contains less than 150 oz. of silver to the ton, and consequently, as very large quantities of

lead are brought into the market containing smaller quantities than this, a large portion of this silver was lost until Hugh Lee Pattinson in the year 1833 obtained a patent for an improved method of separating silver from lead, which soon came into general use and by which large quantities of silver are now extracted from lead.

This method depends upon the fact that if lead containing a small quantity of silver be melted, and the melted mass allowed to cool, a point is reached at which pure lead begins to crystallise out. If the crystals of lead which are thus formed be then withdrawn from the remainder of the metal, and this process continued until the greater part of the lead has been separated, it is found that the liquid which remains contains most of the silver. In order to render this process economical the lead requires to be repeatedly crystallised in a series of iron pots, the lead rich in silver gradually accumulating towards one end of the series, whilst the desilverised or market lead is obtained at the other end.

The melted lead is first thoroughly skimmed, then the fire is withdrawn and the lead allowed to cool, care being taken to break off and mix with the liquid mass any portion that may solidify on the sides of the pot. When the temperature reaches a certain point small crystals of lead begin to form, and at this point the whole mass of metal is continually stirred with an iron rod, whereby the crystals sink to the bottom of the pot and accumulate in considerable quantity. A perforated ladle is now introduced by means of which the crystals are removed. The operation is thus carried on in successive stages until two-thirds or even seven-eighths of the original lead is removed from the pot. By this means in an actual working 846 cwt. of original lead was separated into 36 cwt. of rich lead containing 160 to 170 oz. of silver per ton, and 810 cwt. of poor lead containing 7 to 10 dwt. of silver per ton. The silver is then extracted from the rich lead by the process of cupellation (p 461).

A modification of the Pattinson process, known as the Luce-Rozan process, is now frequently adopted in place of the original method. For this only two pots are necessary, viz., an upper or melting pot, and a lower or crystallising pot. The former holds about 7, and the latter about 21 tons.

The mode of working the plant is as follows[1]: The crystallising pot may be supposed to contain 14 tons of lead crystals from a previous operation, and the melting pot 7 tons of lead of similar silver content, already melted; a moderate fire is set away in the fire-grate of the crystallising pot, and the contents of the melting pot skimmed of their dross; the hot lead from the latter is then run on the warm crystals in the crystallising pot, and with the aid of the moderate fire already referred to, the whole contents of this pot (now 21 tons) are rapidly melted and brought into a working condition, when the charge is carefully skimmed; the melting pot is at the same time charged with 7 tons of lead from a previous operation containing one-half the amount of silver in the lead then being worked up, as this will be the assay of the crystals resulting from the operation about to be performed in the crystallising pot. The fire under the latter is then drawn, and steam at fifty to fifty-five pounds pressure per square inch admitted and distributed evenly by means of a baffle plate. To hasten the cooling and consequent crystallisation, thin streams of water are allowed to run on to the surface of the lead, the crystallisation being more perfect than in the old Pattinson process. As soon as two-thirds of the lead has crystallised out, the rich liquid lead is tapped off, the crystals being retained in the pot by means of perforated plates. The liquid lead is run into moulds and awaits its turn for further treatment. The proportion of silver in the crystals is thus reduced to one-half, whilst that in the liquid run off is doubled, and this process of recrystallising is repeated as in Pattinson's process, until the crystals are sufficiently poor in silver not to require further treatment, and the rich lead is worked up until its silver content is of the standard fit for cupellation.

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[1] Cookson, *Trans. Newcastle Chem. Soc.*, 1878.

This process has the advantage over that of Pattinson that a great saving is effected in fuel and the cost of labour, and also that, except in the case of very hard lead, no further softening process is necessary. The original outlay and expenses for repairs are, however, considerably greater.

Another process for desilverising lead is known as Parkes's or Karsten's zinc process. Molten lead and zinc do not mix in all proportions, lead being capable of taking only 1·6 per cent. of zinc, whilst zinc takes only 1·2 per cent. of lead, and Karsten, in 1842, concluded from experiments which he made on the subject that lead gives up all the silver which it contains if melted with zinc, but he did not apply this conclusion to practical metallurgy. In the year 1850 Alexander Parkes, of Birmingham, patented a process for extracting silver from lead by the above-mentioned reaction. For a ton of lead containing 14 oz. of silver, 22·4 lb. of zinc are needed and a proportionate amount if more silver be present. The alloy of zinc and silver rises to the surface during cooling, and when it solidifies it is withdrawn by means of a perforated ladle. In order to remove the small quantity of zinc which is dissolved in the lead, the mixture is heated to dull redness and steam blown through, the zinc being thereby oxidised, whilst the main portion of the lead remains behind in the marketable state. The zinc–silver alloy is first heated to a temperature slightly above the melting point of lead to liquate as much of the latter as possible, and the residue is heated with carbon in a crucible retort, whereby the zinc is distilled off and collected, the residual rich silver-lead alloy being cupelled in the usual manner.

Gold and copper, which sometimes occur in market lead, can be separated from it in the same way, inasmuch as these metals alloy with zinc even more readily than does silver, and this process has been satisfactorily carried out in England by Baker. A similar method is employed in the Harz; the lead is there melted with 0·16 per cent. of zinc, and the alloy is obtained as a scum on the surface, having the composition :

Pb	Zn	Cu	Ag
89·46	5·78	4·52	0·243

On a second addition an alloy having the following composition is obtained :[1]

Pb	Zn	Cu	Ag
91·05	5·21	3·50	0·238

Market lead almost always contains traces of antimony, copper, and iron, and occasionally of zinc, nickel, and bismuth, whilst the silver which it contains varies from 1 part in 40,000 to 1 part in 200,000, but since the introduction of the method of desilverising by zinc and purification by steam the purity of the commercial lead has very much increased.

Electro-refining of Lead.[2]—Various attempts have been made from time to time to refine lead by an electrolytic process, but until Betts invented his process in 1901, no great success was attained. In this process, the electrolyte consists of lead fluosilicate solution; the anodes are cast of the crude lead and the cathodes of pure lead. In order to obtain solid deposits of ead, *the use of addition agents to the electrolyte is necessary*; and in the process gelatine is mostly used, in the proportion of 1 part of gelatine to 5,000 parts of solution. The impurities remain in the anode slime, and pure lead is deposited at the cathode, as shown by the following table:

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[1] Rammelsberg, *Ber. Entw. Chem. Ind.*, 935.

[2] See *Lead Refining by Electrolysis*, by A. G. Betts (John Wiley & Sons, 1908).

	Cu	Bi	As	Sb	Ag	Pb
Crude lead	1·40	0·14	7·4	4·0	0·64	87·14
Pure lead	0·001	0·0022	0·0025	0·0017		
Anode slime	9·3	0·52	44·58	25·32	4·7	10·3

The following table shows the production of lead in 1919, by the chief lead-producing countries in metric tons: [1]

Australasia	82,732 tons
Belgium	4,157 ,,
Canada	19,566 ,,
France	10,928 ,,
Germany	50,700 ,,
India	19,090 ,,
Italy	16,264 ,,
Mexico	70,229 ,,
Spain	99,912 ,,
United Kingdom	13,100 ,,
United States	385,682 ,,

404 Chemically pure lead is prepared according to Stas [2] as follows:—A solution of acetate of lead is heated in a leaden vessel in contact with thin sheet lead to a temperature of from 40° to 50° in order to precipitate silver and copper. The filtrate is then poured into pure, very dilute sulphuric acid, and the lead sulphate formed carefully washed with a solution of ammonium carbonate and ammonia, and thus converted into lead carbonate. A portion of this is then converted into lead oxide by carefully heating in a platinum basin, whilst to the remaining portion pure dilute nitric acid is added in such quantity that a portion of the carbonate remains undissolved. The oxide of lead is then added to the boiling solution of the nitrate in order to precipitate traces of iron, and the filtered olution poured into one of pure ammonium carbonate. The

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[1] Imperial Mineral Resources Bureau, Statistical Summary, 1921.

[2] *Bull. Acad. roy. Belg.*, 1860, 10, 205.

precipitated lead carbonate is then reduced by means of potassium cyanide, and the metal thus formed fused a second time with the cyanide, when it assumes in the molten state a convex surface like mercury.

Lead, purified by Stas's method, has been distilled in a vacuum at about 1200° in quartz vessels by Lambert and Cullis[1]; before the admission of air it has a brilliant metallic lustre.

Properties and Uses of Lead.—Cohen and others have shown that lead probably exists in two allotropic forms; this has been confirmed by Jänecke, who finds a transition point at about 60° by the study of temperature–pressure curves.[2]

Lead can easily be crystallised in the form of regular octahedra by melting, allowing the molten metal partially to solidify, and pouring off the portion which is still liquid. Similar crystals are obtained by the electrolytic decomposition of solutions of lead salts, using a strong current, but with weak currents plates belonging probably to the monoclinic system are formed. It is also deposited at the cathode by the electrolysis of dilute sulphuric acid with lead electrodes, sometimes in the spongy form consisting of microscopic needles, and sometimes in plates.[3] Similar crystals to these separate out in bright, shining, arborescent forms, known as the lead tree, if a piece of zinc be hung up in a solution of lead acetate. Lead has a specific gravity of 11·254, or, after it has been poured into water, of 11·363. On hammering it cracks and becomes lighter, but if it be pressed it attains a specific gravity of 11·388. Richards and Wadsworth found that lead, purified by recrystallisation of the acetate and the chloride, prepared by electrolysis and fused in pure charcoal vessels in an atmosphere of hydrogen, has a density of 11·367 at 20°.[4] Its atomic heat is 3·06 at −250°, 4·48 at −236°, and 5·70 at −188° (Kamerlingh Onnes and Keesom[5]); at higher temperatures it increases more slowly and Dulong and Petit's law is obeyed. Thus, at −73° it is 6·13, at 0° 6·31, at 136° 6·61. Its average compressibility between 100 and 500 megabars is 0·000,002,2 (Richards and Stull).[6] It is soft and tough, may be cut with a knife, and leaves a streak upon paper. It can easily be rolled out to thin foil, but it cannot be drawn out into fine wire. The presence of antimony, zinc, bismuth, arsenic, and silver increases the brittleness of lead. Lead belongs to the class of white metals, though it has a decidedly bluish-grey tint indicated by the expression lead-grey. A freshly cut surface possesses a bright lustre, which, however, soon becomes dull from superficial oxidation. By the electrolysis of lead nitrate Wöhler obtained a deposit on the negative pole of crystallised leaflets of lead possessing a red colour like that of copper. These did not dissolve in dilute acids, whilst they were soluble in hot nitric acid, and, on dissolving, the colour resembled that of copper to the last moment.[1] Lead melts at 327°, and boils under atmospheric pressure at about 1525° (Greenwood).[2] Its vapour density has been measured at 1870° by von Wartenberg;[3] its molecular weight has been measured by the depression of freezing-point method in mercury solution by Ramsay[4]: from both results it is found to be monatomic.

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[1] *Journ. Chem. Soc.*, 1915, **107**, 210.

[2] *Zeit. physikal. Chem.*, 1915, **90**, 313.

[3] Elbs and Rixon, *Zeit. Elektrochem.*, 1903, **9**, 265; Haber, *Zeit. anorg. Chem.*, 1898, **16**, 438. See also Hughes, *J. Physical Chem.*, 1922, **26**, 316.

[4] *J. Amer. Chem. Soc.*, 1916, **38**, 221.

[5] *Verslag. K. Akad. Wetenschappen*, 1914, **23**, 792.

[6] *Pub. Carn. Inst.*, 1907, 76.

Lead has been obtained in the colloidal form by reducing a solution of the dichloride with hydrazine hydrate in the cold.[5]

Metallic lead is largely employed in the arts for a great variety of purposes on account of its softness and pliability, its low melting point, the difficulty with which it undergoes oxidation at ordinary temperatures, and the fact that it withstands the action of water and of many acids better than most of the common metals.

The most important alloys of lead are those which it forms with tin, which have been described under that metal (p. 880).

COMPOUNDS OF LEAD.

LEAD AND OXYGEN.

405 Lead forms five compounds with oxygen:

Lead suboxide, Pb_2O,
Lead monoxide, PbO,
Lead sesquioxide, Pb_2O_3,
Red lead, Pb_3O_4,
Lead dioxide, PbO_2.

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[1] *Ann. Chem. Pharm. Suppl.*, 1863, 2, 135.

[2] *Proc. Roy. Soc.*, 1909, 82, [*A*], 1560.

[3] *Zeit. anorg. Chem.*, 1908, 58, 320.

[4] *Zeit. physikal. Chem.*, 1889, 3, 359.

[5] Gutbier, *Zeit. anorg. Chem.*, 1902, 31, 448.

The most important of these is the strongly basic monoxide, which corresponds to the chief series of salts, in which lead is divalent. The dioxide acts as a weak basic oxide towards strong acids, as an acidic oxide to strong bases, and also behaves in many respects as a peroxide. The sesquioxide and red lead are probably salts formed by the combination of the basic monoxide and the acidic dioxide (p. 918).

Lead Monoxide, PbO.—This compound was known to the ancients, as it is formed when lead is heated in contact with the air, and is, therefore, produced in various metallurgical processes. The different forms of this compound were, however, regarded as different substances, giving rise to the names *plumbum ustum*, *scoria plumbi*, *scoria argenti*, *galena*, *μολύβδαινα*, *λιθάργυρος*, etc. When lead is heated to its point of volatilisation in the air, it takes fire and burns with a white light, yielding this oxide, which formerly received the name of flowers of lead or *flores plumbi*. Lead, when heated in the air, becomes covered with a grey film, and if the surface be continually renewed, becomes wholly converted into lead-ash, a yellowish-grey, pulverulent mixture of metallic lead and yellow monoxide, which, if heated in the air for a longer time, is wholly converted into the latter. This yellow oxide is termed *massicot*, whilst the other form of lead monoxide, termed *litharge*, is obtained at a temperature at which the oxide fuses, solidifying to a scaly, shining mass sometimes yellowish, sometimes inclined to red.

Crystallised oxide of lead also occurs in nature as a mineral found near Vera Cruz (Nöggerath). The crystals may be artificially obtained by allowing litharge to cool slowly; it forms rhombic octahedra, which are sometimes also found as a deposit in the lead furnaces (Mitscherlich), and red, tetragonal crystals may also be obtained (Geuther). Lead oxide possesses a colour varying from lemon-yellow to reddish-yellow, and on heating assumes a brownish-red tint. Its specific gravity at 4° is 9·36 (Joule and Playfair). It is reduced to the metallic state by carbonic oxide at 100°, by hydrogen at 310°, and by carbon[1] in an atmosphere of nitrogen at 550°. Litharge is largely used in the arts, especially for the manufacture of flint glass, and as a glaze for earthenware; it is used also for the preparation of red lead, lead acetate, lead nitrate, white lead, lead plaster, and drying oils. Commercial litharge contains carbon dioxide and water absorbed from the air, but they may be removed by ignition. Not infrequently it contains small quantities of iron oxide and copper oxide, the latter easily removable by ammonia.

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[1] Doeltz and Graumann, *Metallurgie*, 1907, 4, 420.

Basic Lead Hydroxide, $Pb_2O(OH)_2$.—This substance is obtained as a white precipitate by the action of air and water free from carbonic acid upon the metal, or is thrown down as a white precipitate on the addition of ammonia or a fixed alkali to a lead salt; this, however, dissolves in a large excess of the reagent and the solution contains a *plumbite*, H·PbO·OR, in which the normal hydroxide acts as a weak monobasic acid.[1] The basic hydroxide is obtained in colourless, tetragonal crystals by exposing a cold solution of lead monoxide in caustic potash to the air, the carbon dioxide in the latter converting the caustic potash into potassium carbonate.

The compound $Pb_3O_2(OH)_2$ is formed according to Payen as follows:—100 parts of a solution of basic acetate of lead, $Pb_3O_2(C_2H_3O_2)_2$, saturated at 16°, are added to 50 volumes of cold water which has previously been well boiled: a mixture of 20 parts of ammonia and 30 parts of boiled water is then added, and the solution allowed to stand at 25–30°, when the above hydroxide separates out in glittering octahedra.

At 130° lead hydroxide loses a portion, and at 145° the whole, of its water, being then converted into lead oxide. The hydroxides of lead as well as the oxide turn moistened red litmus paper blue, as they are somewhat soluble in water. They act as strong bases but also combine with certain basic oxides. Thus when lead oxide is fused with the alkalis, alkaline earths, and other metallic oxides, a glass is formed, and, in consequence of this, lead oxide attacks clay crucibles. It dissolves also in caustic potash and soda as well as in lime and baryta water, yielding yellow liquids. The calcium compound is slightly soluble in water, and crystallises in white needles on cooling.

Lead Suboxide, Pb_2O, is formed when lead oxalate is heated in an atmosphere free from oxygen to a temperature below 300° (Dulong):

$$2PbC_2O_4 = Pb_2O + CO + 3CO_2,$$

or when lead oxide is reduced by CO at 300°.[2] It is a black, velvety powder of specific gravity 8·342 at 18° (Tammann),[3] which, when heated in absence of air, or treated with caustic soda or acids, is decomposed into the metal and the monoxide. When lead is melted in the air the surface becomes covered first with a grey film, which, according to Berzelius, consists of the suboxide. The suboxide has by some been considered to be an intimate mixture of finely-divided lead and the monoxide. Against this view, however, is to be placed the fact that mercury does not dissolve metallic lead from this grey powder, whilst a solution of sugar, which readily dissolves lead monoxide, does not take up any from this substance. After heating, dilute acetic acid or a solution of sugar does dissolve out lead oxide, whilst metallic lead remains behind in the coherent state. Cold 10 per cent. sodium hydroxide decomposes it, forming sodium plumbite and metallic lead.

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[1] Hantzsch, *Zeit. anorg. Chem.*, 1902, **30**, 289.

[2] Brislee, *Journ. Chem. Soc.*, 1908, **93**, 154.

[3] *Zeit. anorg. Chem.*, 1901, **27**, 304.

A whole series of monovalent lead salts has recently been described by Denham.[1] By the action of methyl iodide, bromide, and chloride on the suboxide, the corresponding subhalide, PbI, PbBr, or PbCl was obtained. They are sparingly soluble. The subacetate, $PbC_2H_3O_2$, and the subsulphate, Pb_2SO_4, are produced by the action of acetic anhydride and methyl sulphate on the suboxide.

Lead Sesquioxide, Pb_2O_3, is formed when a solution of sodium hypochlorite is carefully added to a cold caustic potash solution of lead oxide (Winkelblech), or when a solution of red lead in acetic acid is precipitated by very dilute ammonia. The action of potassium plumbite on potassium plumbate produces a precipitate of hydrated lead sesquioxide of composition $Pb_2O_3,3H_2O$ or $Pb[Pb(OH)_6]$.[2] It is a reddish-yellow, amorphous powder which does not part with the whole of its water at 150°. It is decomposed by acids into the monoxide and dioxide, and is, therefore, considered to be a compound of these two, PbO,PbO_2, and may be termed *lead metaplumbate*.

Red Lead or *Minium*, Pb_3O_4.—This compound was described by Pliny, under the name of *minium*, but it was at that time not sufficiently distinguished from cinnabar and the red sulphide of arsenic. Dioscorides, however, mentions that it can be prepared from white lead: "*cerussa, si coquatur rufescit*"; and Geber says: "*plumbum aduritur et fit minium.*"

Red lead is usually prepared by carefully heating very finely-divided pure massicot or white lead. For this purpose the oxide is heated for about twenty-four hours either on the flat hearth of a reverberatory furnace, or in barrel-shaped vessels open at both ends, the mass being frequently stirred and the heat not allowed to rise above dull redness (about 400°). The brightness and beauty of the colour depend much on the care spent on the roasting, as these properties are influenced especially by the particular molecular condition of the material, and this is produced only at a given temperature.

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[1] *Journ. Chem. Soc.*, 1917, **111**, 29; 1918, **113**, 249; 1919, **115**, 109.

[2] Bellucci and Parravano, *Zeit. anorg. Chem.*, 1906, **50**, 107.

Red lead is a scarlet, crystalline, granular powder, which, on heating, first assumes a finer red colour and afterwards turns violet, and lastly black, but on cooling regains its original tint. When more strongly heated, at about 470°,[1] it loses oxygen and is converted into the monoxide. Its specific gravity varies from 8·6 to 9·1. Commercial red lead frequently contains the yellow oxide, litharge, mixed with it, which may be extracted by repeatedly digesting with a solution of lead acetate. Red lead is largely used as a paint and also in the preparation of flint glass. For both these purposes it is necessary that it should be as free as possible from iron, and in this case it is not infrequently prepared from white lead. Red lead is also adulterated with oxide of iron, red bole, powdered heavy spar, and brick dust. These substances remain undissolved when red lead is digested in warm dilute nitric acid to which a little sugar has been added, whilst the red lead is dissolved completely. Boiling hydrochloric acid extracts sesquioxide of iron from the impure oxide with formation of lead chloride and liberation of chlorine. Like the sesquioxide, it is decomposed by acids into the monoxide or a corresponding salt, and the dioxide, and is therefore regarded as a compound of two molecules of the former and one of the latter, $2PbO,PbO_2$, and may be termed *lead orthoplumbate.*

Lead Dioxide, Lead Peroxide, or *Puce-coloured Oxide of Lead,* PbO_2.—This substance was discovered by Scheele, who observed that red lead is coloured brown when treated with chlorine water, whilst Priestley found that nitric acid produces the same reaction. The properties of the puce-coloured lead oxide were more exactly examined by Proust and Vauquelin.

Lead dioxide may be prepared according to a variety of methods. The simplest plan is to act upon red lead with dilute nitric acid:

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

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[1] Milbauer, *Chem. Zeit.*, 1909, 33, 950, 960.

It is likewise obtained by the action of chlorine upon lead salts in the presence of alkalis (Wöhler), or by treating a hot solution of a pure lead salt with a soluble hypochlorite (Böttger):

$$PbO + NaClO = PbO_2 + NaCl.$$

It is also prepared by the electrolysis of a solution of sodium chloride, in which litharge is suspended.[1]

It is obtained in the dry way by fusing 4 parts of lead monoxide, 1 part of potassium chlorate, and 8 parts of nitre (Liebig and Wöhler). Lead oxide is also converted into the dioxide by the action of ozone as well as of hydrogen peroxide. It is deposited at the positive pole when a solution of a lead salt in nitric acid is decomposed electrolytically.[2]

This substance is found native in the form of plattnerite, which crystallises in black, hexagonal prisms having a specific gravity of 9·4. The artificial dioxide sometimes assumes the orm of brownish-black, six-sided tablets, but generally consists of a dark brown powder having a specific gravity of 8·9 to 9·2.

Lead dioxide decomposes on heating into oxygen and the monoxide. It loses oxygen when simply exposed to sunlight, ed lead being formed. It has a strongly oxidising action, and when triturated with one-sixth of its weight of sulphur, it takes ire and burns with a brilliant flame, forming sulphide of lead.[3] Aqueous hypophosphorous acid is at once oxidised with formation of lead phosphate. When exposed to sulphur dioxide at ordinary temperatures it becomes red hot and is converted into lead sulphate, whilst nitrogen peroxide and even ammonia convert it into lead nitrate. A large number of organic acids and other carbon compounds when triturated with it likewise cause evolution of light and heat. When treated with hydrochloric acid, chloride of lead and free chlorine are formed.

Lead dioxide is often employed as an oxidising agent, as, for instance, in the analysis of organic substances containing sulphur, in order to separate the sulphur dioxide from carbon dioxide. The mixture of nitrate and dioxide, termed oxidised red lead, obtained by treating red lead with nitric acid, is employed in the manufacture of lucifer matches.

Lead dioxide is capable of acting as a weak basic oxide, yielding the unstable tetravalent lead salts, and also as a peroxide and an acid-forming oxide, forming compounds to which the name *plumbates* has been given. *Orthoplumbates* having the composition $M^{I}_4PbO_4$ and *metaplumbates*, $M^{I}_2PbO_3$, are known,[1] and the free *metaplumbic acid*, $PbO(OH)_2$ or H_2PbO_3, is deposited at the positive pole as a black, lustrous substance on the electrolysis of a slightly alkaline solution of lead sodium tartrate.

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[1] *Chemische Fabrik, Griesheim-Elektron*, German Patent, 124512.

[2] Wolman, *Zeit. Elektrochem.*, 1897, 3, 537; Hollard, *Compt. rend.*, 1903, 136, 229, and others.

[3] Vauquelin, *Ann. Chim. Phys.*, 1807, 62, 221.

The orthoplumbates of the alkaline earths are obtained by heating the carbonates or hydroxides with lead monoxide in presence of air, the *calcium* salt, Ca_2PbO_4, crystallising with four molecules of water in almost colourless, microscopic, transparent crystals. These compounds evolve oxygen on strongly heating, and it has been proposed to utilise this method for obtaining oxygen from the atmosphere on the large scale; the calcium salt has also been used as an oxidising agent.[2]

The hydrosol of hydrated lead peroxide (plumbic acid) has been prepared by the dialysis of potassium plumbate.[3]

Potassium Metaplumbate, $K_2PbO_3,3H_2O$, is obtained in crystals by fusing lead dioxide with excess of caustic potash in a silver crucible, dissolving in water, and evaporating in a vacuum.[4] The solution gives with most metallic salts precipitates of the corresponding metaplumbates.

Calcium Metaplumbate, $CaPbO_3,4H_2O$, is obtained by digesting the orthoplumbate with sodium peroxide and water, and from this other metaplumbates have been obtained.[5]

As already mentioned, lead sesquioxide and red lead may be regarded as the metaplumbate and orthoplumbate of lead, their constitution being represented by the formulæ $Pb^{II}PbO_3$ and $Pb_2^{II}PbO_4$. Lead metaplumbate has been prepared from the calcium salt and is identical with the sesquioxide.[6]

When calcium meta- or ortho-plumbate is heated in dry air at 250°, *calcium perplumbate*, $CaPb_2O_6$, is formed.[7]

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[1] Compare Bellucci, *Atti R. Accad. Lincei*, 1905, [5], **14**, i., 457.

[2] Kassner, *Arch. Pharm.*, 1890, **228**, 109; 1894, **232**, 375; 1895, **233**, 501.

[3] Bellucci and Parravano, *Atti R. Accad.* Lincei, 1906, [5], **15**, ii., 542.

[4] *Ann. Chim. Phys.*, 1844, [3], **12**, 400.

[5] Grützner and Höhnel, *Arch. Pharm.*, 1895, **233**, 512.

[6] Höhnel, *Arch. Pharm.*, 1895, **233**, 501.

[7] Kassner, *Arch. Pharm.*, 1899, **237**, 409; 1900, **238**, 449.

LEAD AND HYDROGEN AND THE HALOGENS.

406 *Lead Hydride.*—The existence of a volatile hydride of lead was first suspected from the behaviour of one of its radioactive isotopes. Attempts to prepare this compound from ordinary (non-radioactive) lead, by the action of acids on its magnesium alloy, failed: but Paneth and Norring have succeeded in obtaining it by a combined electrolysis-spark process. The electrode gases contain small amounts of a volatile hydride of lead of unknown composition, which can be condensed by liquid air and which re-evaporates without decomposition. When passed through a heated Marsh tube, it is decomposed, with the formation of a dull grey deposit of lead.[1]

Lead Fluoride, PbF_2.—This compound is obtained by heating lead oxide or carbonate with hydrofluoric acid, or by precipitating a lead salt with a soluble fluoride. It is a white powder, almost insoluble in water and in hydrofluoric acid, but fairly soluble in hydrochloric and nitric acids. When treated with ammonia, an easily soluble basic fluoride is formed. If a solution of lead chloride be precipitated with sodium fluoride, the compound PbClF is formed. The formation of this compound has been confirmed by the thermal analysis of the system $PbCl_2$-PbF_2,[2] and a second compound, $PbCl_2,4PbF_2$, detected. The chloro-fluoride of lead (PbClF) is slightly soluble in water, dissolving without decomposition (Berzelius).

Lead Tetrafluoride, PbF_4.—This compound is probably formed by the action of strong sulphuric acid on the acid plumbifluoride, $3KF,HF,PbF_4$, but has not been obtained in the pure state. The foregoing double salt, which is isomorphous with the analogous tin derivative, is obtained by the action of hydrofluoric acid and potassium fluoride on lead tetracetate, or by fusing lead dioxide with potassium fluoride and treating the product with hydrofluoric acid. It forms monoclinic needles which evolve hydrogen fluoride at 230°, and at a higher temperature yield free fluorine.[3]

Lead Chloride, $PbCl_2$.—Dioscorides mentions that yellow oxide of lead when brought in contact with common salt and warm water becomes white. After the discovery of silver chloride, to which the name of horn-silver was given, the corresponding lead compound was termed horn-lead (*plumbum corneum*). Lead chloride occurs native in the craters of volcanoes as the mineral cotunnite. Lead combines with chlorine, but slowly, and without incandescence. Dilute hydrochloric acid dissolves the metal only in the presence of air, and then but slowly. The boiling concentrated acid, however, converts it into chloride with evolution of hydrogen gas. Lead chloride is easily prepared by the action of hydrochloric acid on the oxide or carbonate, and also by the precipitation of a tolerably concentrated solution of a lead salt by means of hydrochloric acid or a soluble chloride. It is thus obtained in the form of a white, crystalline precipitate, of which 100 parts of water dissolve 0·909 part at 15°, and 3·2 parts at 100°. The salt crystallises, when a boiling solution is cooled, in white, silky, rhombic needles, having a specific gravity of 5·8. It is less soluble in dilute hydrochloric acid and solutions of chlorides than in pure water, but dissolves more freely in concentrated hydrochloric acid; hence a precipitate may be obtained by adding water to the latter solution, whilst the aqueous solution is precipitated by hydrochloric acid. It also dissolves readily in the solutions of the acetates and thiosulphates of the alkali metals. When heated in absence of air, lead chloride melts at about 485°, solidifying on cooling to a white, translucent, horny mass; it volatilises at a temperature of 861-934°, the vapour having a density of 5·8, corresponding to the formula $PbCl_2$.[1]

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[1] *Ber.*, 1920, 53, [*B*], 1693. See also Paneth, Matthies, and Schmidt-Hebbel, *Ber.*, 1922, 55, [*B*], 775.

[2] Sandonnini, *Atti R. Accad. Lincei*, 1911, [5], 20, i., 172.

[3] Brauner, *Journ. Chem. Soc.*, 1894, 65, 393.

Lead yields a large number of oxychlorides. The compound $PbCl_2,PbO$ occurs as the mineral matlockite, and may be obtained artificially by igniting the chloride in the air till no further fumes are evolved. The mineral mendipite has the composition $PbCl_2,2PbO$, and numerous others, some of which contain water of crystallisation, have been prepared. Ruer[2] has examined the freezing points of mixtures of lead oxide and lead chloride, and has obtained evidence of the existence of the compounds, $PbCl_2,PbO$, $PbCl_2,2PbO$, and $PbCl_2,4PbO$. The hydrate $PbCl_2,PbO,H_2O$, which may also be formulated as lead hydroxychloride, $Pb(OH)Cl$, and occurs as the mineral laurionite, was formerly prepared by a process patented by Pattinson in 1849. In this process chloride of lead is first prepared from finely pulverised galena and concentrated hydrochloric acid;—this is then dissolved in water and mixed with lime-water in certain definite proportions; a snow-white precipitate having the composition given above is thrown down, which was at one time used as a paint in place of white lead.

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[1] Roscoe, *Proc. Roy. Soc.*, 1878, 27, 428.

[2] *Zeit. anorg. Chem.*, 1906, 49, 365.

A hydrated oxychloride is likewise obtained by warming lead oxide with a solution of common salt (Scheele), caustic soda being produced at the same time. In the year 1787 Turner took out a patent for the purpose of preparing caustic soda by the reaction, and found that the residue when heated became anhydrous and possessed a yellow colour. This oxychloride is known under the name of *Turner's yellow* or *patent yellow.* Vauquelin then showed that when lead chloride and lead oxide are fused together, a yellow-coloured body is obtained. This is known as *Cassel yellow*, and is prepared by fusing together 1 part of ammonium chloride and about 10 parts of massicot, minium, or white lead; a part of the ammonium chloride sublimes undecomposed, and the resulting compound contains about one molecule of chloride to seven molecules of oxide, part of the lead being at the same time reduced by the ammonia.

Lead chloride also yields a number of double salts with the chlorides of other metals.

Lead Tetrachloride, $PbCl_4$.—A solution of this compound is obtained by dissolving the dioxide in well-cooled hydrochloric acid, but it is best prepared by passing chlorine into lead dichloride suspended in hydrochloric acid. On addition of ammonium chloride, *ammonium plumbichloride*, $(NH_4)_2PbCl_6$, crystallises out, and the same compound is also formed by acting on lead tetracetate with concentrated hydrochloric acid and then adding ammonium chloride.[1] It may also be obtained by the action of hydrochloric acid and ammonium persulphate on lead chloride in the cold,[2] or by the electrolysis of concentrated hydrochloric acid with lead electrodes, the cathode being placed in a porous pot, when an orange solution of H_2PbCl_6 is formed, and this on addition of ammonia yields the above compound.[3] When this compound is added to well-cooled sulphuric acid, it yields the tetrachloride, as a yellow, refractive, fuming liquid, which readily decomposes into the dichloride and chlorine. It has a specific gravity of 3·18 at 0°, solidifies at $-15°$ to a yellowish, crystalline mass, and yields a hydrate with a small quantity of water, but in presence of an excess is decomposed into lead dioxide and hydrochloric acid.[1]

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[1] Hutchinson and Pollard, *Journ. Chem. Soc.*, 1896, **69**, 212.

[2] Seyewetz and Trawitz, *Compt. rend.*, 1903, **136**, 686.

[3] Elbs and Nübling, *Zeit. Elektrochem.*, 1903, **9**, 776.

Lead Bromide, $PbBr_2$.—This compound closely resembles the chloride. It is obtained by treating lead oxide with aqueous hydrobromic acid, or by precipitating a lead salt with a solution of potassium bromide, when it is thrown down in the form of white, shining needles. It dissolves in hot water, and has a specific gravity of 6·6. When heated in a closed vessel it fuses, forming a red liquid which on cooling solidifies to a white, horny mass. Fused in contact with the air, it emits white fumes and leaves a residue of *oxybromide*, $PbBr_2,PbO$, forming a pearly, yellow mass, whilst the *hydrated oxybromide*, $PbBr_2,PbO,H_2O$, or $PbBrOH$, has been prepared by heating a mixture of solutions of sodium bromide and lead acetate.[2]

Lead Iodide, PbI_2.—Hydriodic acid easily dissolves lead, and the iodide separates out from a concentrated solution in beautiful yellow crystals (Deville). When a solution of lead salt is mixed with a soluble iodide, a yellow precipitate of lead iodide is formed. This is soluble in 1,235 parts of cold and 194 parts of boiling water, giving rise to a colourless solution from which the iodide separates out on cooling in yellow laminæ resembling those of mosaic gold. The specific gravity of this compound is 6·1; on heating, it becomes reddish-yellow, then bright red, and lastly brownish-black; it melts in a closed tube to a reddish-brown liquid which solidifies to a yellow, crystalline mass, and may be sublimed unchanged by heating in carbon dioxide.[3] Like the chloride and bromide, it forms basic salts.

A number of mixed halogen compounds of lead have been described, which are mostly prepared by the action of the halogen salts of potassium or ammonium on those of lead. In this way the compounds $PbFBr$, $PbICl$, and $PbBrCl$ are stated to be formed, as well as double compounds of these with the halogen salts of ammonia.[4] There is, however, some doubt as to whether these are true compounds or isomorphous mixtures.[5]

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[1] Friedrich, *Monatsh.*, 1893, **14**, 505; Classen, *Zeit. anorg. Chem.*, 1893, **4**, 100.

[2] de Schulten, *Bull. Soc. franç. Min.*, 1897, **20**, 186.

[3] Schtscherbakoff, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 682.

[4] Thomas, *Compt. rend.*, 1898, **126**, 1349; 1899, **128**, 1234; 1329, *Bull. Soc. chim.*, 1898, [3], **19**, 598; Fonzes-Diacon, *ibid.*, 1897, [3], **17**, 346.

[5] Herty and Bogg, *J. Amer. Chem. Soc.*, 1897, **19**, 820.

LEAD AND SULPHUR.

407 *Lead Sulphide*, PbS, occurs in nature as galena, crystallised in cubes or in other combinations of the regular system. It possesses a bluish-grey colour, and has a specific gravity varying from 7·25 to 7·7. This mineral was known to the ancients under its present name, but the fact that it contained sulphur was not recognised until after some time. Thus even Kunkel was unacquainted with this fact, though Boyle[1] was aware that when galena is heated with scrap iron metallic lead is formed, and recommended this mode of producing lead.

When sulphur vapour is led over metallic lead it takes fire and burns, forming a crystalline sulphide; even tolerably thick strips of lead take fire in sulphur vapour, depositing half-fused globules of lead sulphide. It can also be prepared by fusing lead oxide with an excess of sulphur. When sulphuretted hydrogen is passed into a solution of lead nitrate, an amorphous, black precipitate is formed, but if the gas be passed into a dilute solution of the salt containing nitric acid a crystalline precipitate is obtained, consisting of microscopic cubes (Muck).

Sulphide of lead fuses at a strong red heat—at 1120° ± 10° according to Friedrich[2]—and when heated in a current of many gases sublimes in cubes which often have a diameter of 1·5 mm. Crystals of galena are often obtained in lead works in a similar way. On the other hand, octahedral crystals may be obtained by fusing 1 part of the precipitated sulphide with 6 parts of potash and 6 parts of sulphur (Schneider). Nitric acid converts galena, with separation of sulphur, partly into the nitrate and partly into the sulphate, the latter compound being formed in the largest quantity when the acid is strongest. Hot concentrated hydrochloric acid dissolves it with evolution of sulphuretted hydrogen.

When an aqueous solution of a lead salt containing an excess of hydrochloric acid is treated with a small quantity of sulphuretted hydrogen a yellowish- to dark-red precipitate is obtained which consists of a double chloride and sulphide of lead. According to Hünenfeld,[3] this precipitate has the composition $3PbS,2PbCl_2$, whilst Parmentier[4] found the composition $PbS,PbCl_2$; it is converted by an excess of sulphuretted hydrogen into lead sulphide, and loses lead chloride on treatment with hot water. The compound $PbS,4PbCl_2$ has been obtained by diluting a solution of lead sulphide in concentrated hydrochloric acid, whilst similar compounds with lead bromide and iodide have also been prepared.[1]

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[1] *A hydrostatical way of estimating ores of lead.*

[2] *Metallurgie*, 1907, **4**, 479; 1908, **5**, 23.

[3] *J. pr. Chem.*, 1836, 7, 27.

[4] *Compt. rend.*, 1892, **114**, 299.

A polysulphide of lead, PbS_5, is formed by the action of calcium polysulphide on lead nitrate at 0°, as a purplish-red precipitate which decomposes rapidly at ordinary temperatures into the monosulphide and sulphur.[2]

Lead Sulphate, $PbSO_4$.—This substance is found native as lead vitriol or anglesite in transparent, rhombic crystals, isomorphous with those of celestine and heavy-spar, or as pseudomorphs of galena. It is obtained as a white powder by precipitating a lead salt with sulphuric acid or a soluble sulphate. If a layer of water be poured on to a saturated solution of potassium sulphate, and a platinum wire on which some lead chloride has been fused allowed to dip into the water, crystals of lead sulphate are gradually formed.[3] It may also be formed by the action of sulphur dioxide on lead peroxide.[4] Lead sulphate has a specific gravity of 6·2 to 6·3. It melts at about 1100° withou decomposition. One part of the salt dissolves in 21,739 part of cold water, 12,135 parts according to Schnal,[5] and in 36,50 parts of dilute sulphuric acid, whilst concentrated sulphuric aci can take up about 6 per cent, of the compound. It also dissolve in warm ammonia and caustic potash, and in hot hydrochlori acid with formation of lead chloride. Sulphate of lead is likewis very readily soluble in ammoniacal salts, especially in the acetate; calcium acetate and many other salts also dissolve it.

When lead sulphate is boiled with concentrated sulphuric acid, it is dissolved and is afterwards deposited in crystals, and if the mother-liquor be allowed to stand in contact with moist air crystals of the acid sulphate, $PbSO_4,H_2SO_4,H_2O$, similar to those of the corresponding barium salt, are formed.

When the normal salt is treated with ammonia the basic sulphate, Pb_2SO_5 or $O{<}^{Pb\cdot O}_{Pb\cdot O}{>}SO_2$, is formed. The same salt is obtained in microscopic needles when an excess of a hot solution of sodium sulphate is added to basic lead formate (Barfoed).

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[1] Lenher, *J. Amer. Chem. Soc.*, 1895, **17**, 511; 1901, **23**, 680.

[2] Bodroux, *Compt. rend.*, 1900, **130**, 1397.

[3] Manross, *Annalen*, 1852, **82**, 360.

[4] Marino, *Zeit. anorg. Chem.*, 1907, **56**, 233.

[5] *Compt. rend.*, 1909, **148**, 1394.

The basic sulphates, $PbSO_4,2PbO$ and $PbSO_4,3PbO$, also exist.[1]

Lead Persulphate, $Pb(SO_4)_2$, is obtained at the anode as a greenish-yellow, crystalline precipitate when a solution of sulphuric acid is electrolysed below 30° with an anode of lead placed in a porous pot. It is decomposed by water with formation of sulphuric acid and lead dioxide, and is a powerful oxidising agent.[2]

Lead Subsulphate, Pb_2SO_4, has been prepared.[3]

LEAD AND NITROGEN AND PHOSPHORUS.

408 *Lead Imide*, PbNH, is obtained by the action of potassamide on lead iodide in liquid ammonia, and is a reddish-brown, explosive substance. If the lead iodide be in excess, the white basic salt, NPb_2I,NH_3, is obtained. Lead imide reacts with potassamide in liquid ammonia at low temperatures to form potassium ammono-plumbite, $KNPb,2\frac{1}{2}NH_3$, which loses half a molecule of ammonia at $-40°$ to form the compound $KPb(NH_2)_3$. At 60°, a further molecule of ammonia is lost with the production of the explosive compound $KNPb,NH_3$. If these substances are treated with ammonium iodide in liquid ammonia the successive products are lead imide, an ammonobasic lead iodide, $Pb_2(NH_2)_3I$, and lead iodide. Lead imide is an amphoteric electrolyte in liquid ammonia.[4]

Lead Nitrite, $Pb(NO_2)_2$.—This substance is most readily obtained by decomposing silver nitrite with lead chloride and concentrating the solution in a vacuum, when yellow prisms separate out which are easily soluble in water. On evaporating the solution, nitric oxide is evolved, and a basic salt remains behind. If lead nitrate be digested with water in contact with finely-divided metallic lead for a few hours at a temperature of 75°, a yellow solution is formed, which on cooling deposits the basic double salt, $Pb(NO_3)OH,Pb(NO_2)OH$, in glittering yellow plates. Proust, who first obtained this compound, considered it to be a nitrate of a suboxide of lead, whilst Berzelius viewed it as a simple basic nitrite. If its solution be boiled with metallic lead and a large quantity of water, orange-yellow prisms separate out on cooling, having the composition $Pb(NO_2)_2,Pb(NO_3)_2,5PbO,3H_2O$. This salt was formerly termed

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[1] Schenck and Rassbach, *Ber.*, 1908, **41**, 2917.

[2] Elbs and Fischer, *Zeit. Elektrochem.*, 1900, **7**, 343.

[3] Denham, *Journ. Chem. Soc.*, 1919, **115**, 109.

[4] Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820; and *J. Physical Chem.*, 1911, **15**, 509.

lead hyponitrate. If lead nitrate be boiled with one and a half times its weight of lead and fifty times its weight of water for twelve hours in a long-necked flask, pale red needles of basic nitrite of lead, $Pb(NO_2)_2,3PbO,H_2O$, are formed. Other basic nitrites of lead are known.[1]

Lead Nitrate, $Pb(NO_3)_2$.—Lead nitrate is first mentioned in the *Alchymia* of Libavius. It is here termed *calx plumb. dulcis.* "Fit per aquam fortem comminuto plumbo affusam vase in aqua frigida locato. Fit instar crystallorum." Lead dissolves slowly in warm dilute nitric acid. Lead nitrate, or lead saltpetre, as it is sometimes called, is prepared on the large scale by dissolving lead scale or litharge in hot dilute nitric acid, having a specific gravity of 1·35. The solution is evaporated until it attains a specific gravity of 1·6, and is then allowed to cool in earthenware vessels, when the salt separates out in milk-white, regular octahedra exhibiting a combination of the regular dodecahedron. If a cold solution of the salt be allowed to undergo spontaneous evaporation, transparent octahedral crystals are formed (Knop). It has a specific gravity of 4·5, and on dissolving in water gives rise to a reduction of temperature; 100 parts of water dissolve, according to Mulder, as follows:

At	0°	10°	20°	40°	60°	80°	100°
$Pb(NO_3)_2$	36·5	44·4	52·3	69·4	88·0	107·6	127·0

It scarcely dissolves in strong alcohol and is only slightly soluble in aqueous alcohol. Its aqueous solution is precipitated by nitric acid. It has an astringent, metallic taste, decrepitates when heated, detonates with brilliant sparks when thrown upon red-hot charcoal, and deflagrates when triturated with sulphur. When heated in a sealed tube at 357°, it decomposes partially according to the equation:[2]

$$Pb(NO_3)_2 \rightleftarrows PbO + O + 2NO_2.$$

The salt is largely used in dyeing and calico-printing, for the preparation of mordants and of chrome-yellow.

When the normal salt is boiled with an equal weight of lead oxide and water, crystals of a basic nitrate, $Pb(NO_3)OH$, are thrown down on cooling. These are sparingly soluble in cold and more readily soluble in hot water. When gently heated it is converted into red lead. If a solution of the normal salt be precipitated with a slight excess of ammonia, and the solution heated in a closed vessel with the addition of some of the normal salt until the smell of ammonia has almost disappeared, a basic nitrate is formed, having the composition $2Pb(NO_3)OH,PbO$. It is a white powder slightly soluble in water. When an excess of ammonia is employed the compound $Pb(NO_3)OH,2PbO$ is thrown down as a white powder.

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[1] Compare Chitesotti, *Atti R. Accad. Lincei*, 1908, [5], **17**, ii., 377 and 474.

[2] Baekeland, *J. Amer. Chem. Soc.*, 1904, **26**, 391; Morgan, *J. Physical Chem.*, 1904, **8**, 416.

Phosphates of Lead.—When common sodium phosphate is precipitated by acetate of lead a white precipitate of normal lead orthophosphate, $Pb_3(PO_4)_2$, is formed. If a boiling solution of lead nitrate be precipitated by phosphoric acid, a glittering white, crystalline precipitate of $HPbPO_4$ is produced, and the same compound is obtained in the form of crystalline needles when lead pyrophosphate is heated with water to 250°. The pyrophosphate and metaphosphate of lead are white precipitates.

The following minerals are lead phosphates and arsenates isomorphous with apatite:

Pyromorphite, $Pb_3(PO_4)_2,Pb_2Cl(PO_4)$,
Polysphærite, $(Pb,Ca)_3(PO_4)_2,(Pb,Ca)_2Cl(PO_4)$,
Mimetite, $Pb_3(AsO_4)_2,Pb_2Cl(AsO_4)$,
Campylite, $Pb_3[(As,P)O_4]_2,Pb_2Cl[(As,P)O_4]$.

Some of the chlorine is usually replaced by fluorine.

Borates of Lead.—If boron trioxide and lead oxide be fused together in the proportion of two molecules of the former to three of the latter, a yellowish soft glass is obtained, which softens when exposed to the action of hot oil. If double the weight of boron trioxide be employed the glass obtained is harder and less coloured, and if three times the weight be used a colourless glass is obtained, which possesses the hardness of flint glass and refracts light much more powerfully.[1] When a lead salt is precipitated with borax, a compound having the composition $Pb_2B_6O_{11},4H_2O$ is formed, and this when warmed with strong ammonia is converted into a heavy, white powder having the composition PbB_2O_4,H_2O, which again, when boiled with a solution of boric acid, yields amorphous $PbB_4O_7,4H_2O$.[2]

LEAD AND CARBON AND SILICON.

409 *Carbonates of Lead.*—*Normal Lead Carbonate*, $PbCO_3$, occurs as cerussite or white carbonate of lead in rhombic crystals

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[1] Faraday, "On the Manufacture of Optical Glass," *Phil. Trans.*, 1830, 120, 1.

[2] But see also, Thompson, *Trans. Engl. Ceram. Soc.*, 1918–19, 18, 510.

isomorphous with aragonite, and also as pseudomorphs of galena and lead sulphate. The same compound is formed by precipitating a cold solution of lead acetate by ammonium carbonate (Berzelius), or by passing carbon dioxide into a dilute solution of lead acetate (Rose). Cerussite forms colourless, transparent, lustrous crystals, having a specific gravity of 6·46, whilst the precipitated carbonate has a specific gravity of 6·43. It is scarcely soluble in water, one part dissolving in 50,500 parts of water at the ordinary temperature, but in presence of ammoniacal salts it is somewhat more soluble (Fresenius). A solution of carbon dioxide in water also dissolves it slowly.

Lead forms several basic carbonates, among which *white lead* is the most important, since it is manufactured on a very large scale. In the pure state this compound consists of $2PbCO_3,Pb(OH)_2$, but the commercial product usually contains the normal carbonate in addition.

White Lead has long been known, being called ψιμύθιον by Theophrastus. The process of manufacture as described by him consisted in the action of vinegar on lead, the material formed being scraped off after a time from the surface of the metal. Pliny mentions the same subject under the name of *cerussa* and describes the above method of manufacture. He also states that it may be obtained by dissolving lead in vinegar and evaporating to dryness. Thus it would appear that the difference between white lead and sugar of lead was not known. The Latin Geber describes the manufacture as follows: "plumbum ponendo super vaporem aceti fit cerussa," a description which accords with the method employed even up to the present day. For some time white lead was supposed to be a compound of calx of lead with vinegar, and it was not until 1774 that Bergman showed that white lead contained lead calx and fixed air, and gave to it the name of "luftsaurer blei-kalk" or "calx plumbi ærata."

The oldest process for the manufacture of white lead is known as the *Dutch process*. In this method conical glazed earthenware pots, 8 inches wide, are filled to one-fourth of their depth with malt vinegar. At one-third of the height of the pot from the bottom are three projecting points on which a cross-piece of wood is laid, and on this are placed vertically a number of thin leaden plates rolled up into a spiral, and the whole is covered with a leaden plate, which often has holes punched in it. The pots are then placed under a shed in rows upon horse dung or spent tannery bark and covered with boards; another layer of dung or decomposing bark is laid upon the boards, and on this another row of pots, many rows of pots being thus placed above one another, and the whole covered by the tan or dung. By the slow oxidation of the dung heat is evolved, which assists the evaporation of the vinegar and causes basic lead acetate to be formed, and this in contact with the carbon dioxide evolved from the putrefaction of the organic matter is converted into white lead. In the course of from four to five weeks the greater portion of the lead is converted into white lead, the change taking place from without inwards. The white lead is then detached, ground into a fine paste whilst moist, washed well to free it from adhering acetate, and dried in small round pots. Unwashed white lead contains a considerable quantity (from 2 to 12 per cent.) of the normal acetate.

To reduce the risk of poisoning attending the drying of the white lead pulp, formed by the treatment of the corroded lead with water, it is customary in some works to dry the pulp in ovens in which a vacuum is maintained. A further improvement, applicable in the manufacture of paint, is that described by Ismay (English Patent 23969, 1895) in which the white lead pulp is mixed with oil in a pug mill; in this way the greater portion of the water is displaced by the oil, and the last portion is driven off from the paint by surrounding the mill with a heating jacket so arranged that the contents are heated in a partial vacuum. In this way the use of drying stoves and the dangers attending it are completely obviated.

According to the *German method* of manufacture, plates of lead are hung up in wooden boxes placed in an atmosphere of carbon dioxide in heated chambers containing a stratum of acetic acid, or the plates are suspended in heated chambers having their floors covered with tan and acetic acid.

The *French method*, introduced by Thénard, and the *English method*, suggested by Benson, do not furnish a white lead which possesses the same covering power as that prepared by the other methods. The process in these cases consists in passing carbon dioxide through a solution of a basic acetate of lead, obtained by boiling a solution of lead acetate with litharge.

Another method, which yields a white lead of excellent covering power, is the process patented by Dale and Milner. This consists in carefully grinding between millstones a mixture of litharge, or any insoluble basic lead salt, with water and sodium bicarbonate. Milner has improved upon this method by grinding a mixture of 4 parts of finely-divided litharge with 1 part of common salt and 16 parts of water. After about 4½ hours the reaction is complete. The mixture of basic lead chloride and caustic soda is then brought into a leaden vessel, well stirred with a wooden pestle and a current of carbon dioxide passed through it until the liquid is neutral. If the carbon dioxide be passed in too long the product is spoiled.[1]

Another process, called, after its discoverer, the *Bischof process*, is now employed on a large scale at Mond's works at Brimsdown in Middlesex.[2] Metallic lead is converted into litharge, and the latter is heated at 250–300° in a stream of water gas. It is thereby reduced to a black suboxide of unknown composition, and this is treated with water, when a yellow hydrate is formed with evolution of heat, which is further converted into white lead by treatment with carbon dioxide. This process, besides being rapidly completed, has the advantage of being carried out mechanically, and in such a manner that there is no dust, and thus a great source of danger to the workers is avoided. The product has a composition practically identical with that formed by the German process.

Several electrolytic processes have been proposed, but only a very small amount of white lead is produced by this means.[3]

White lead is a white, earthy, heavy, amorphous powder which appears under the microscope to consist of round, transparent globules of the size of from 0·00001 to 0·00004 of an inch in diameter. The specific gravity of that prepared by the Dutch method is somewhat greater than that prepared by the French method, and it therefore absorbs less oil or varnish and gives rise to a thicker colour.

Although it acts as a powerful poison, and is turned black by sulphuretted hydrogen, white lead is still almost exclusively used as the basis of paint, and has been replaced only to a very small extent by zinc-white or baryta-white. This is accounted for by the fact that it possesses a much greater covering power and is much more opaque than either of the other two.

White lead is often mixed with heavy-spar and gypsum. A mixture of equal parts of white lead and barium sulphate is known as *Venetian white*, whilst *Hamburg white* is a mixture of one part of white lead to two of barium sulphate, and *Dutch white* of one part to three of barium sulphate. The amount of this admixture may be readily ascertained by treating a weighed portion of the powder with warm dilute nitric acid, when the barium sulphate remains behind.

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[1] Patent No. 4063, 22nd November, 1875.

[2] Caro, *Verh. des Vereins zur Beförderung des Gewerbfleisses, Berlin*, 1906.

[3] Luckow, D.R.-P., 91707 and 105143; Browe and Chaplin U.S.P., 551361, 1895 and 555292, 1896.

Lead Cyanide, $Pb(CN)_2$, is obtained as a white powder when a solution of a normal lead salt is mixed with potassium cyanide. It is not soluble in the cyanides of the alkali metals and is decomposed on the addition of an acid. When heated in a closed vessel a mixture of lead and charcoal remains behind which, if it has not been too strongly heated, is pyrophoric.

Lead Cyanate, $Pb(CNO)_2$, is obtained by mixing solutions of a cyanate and of a soluble lead salt. A dense white precipitate is thrown down, which soon assumes the form of slender needles like chloride of lead. Under the action of boiling water lead cyanate is readily and quantitatively hydrolysed into lead carbonate and urea.[1]

Silicates of Lead.—Silica fuses with lead oxide to form a yellow glass, and silicates obtained by "fritting" lead oxide with siliceous material are used by potters for preparing glazes. Glass formed of equal parts of lead oxide and silica does not become dull when it is exposed to the action of sulphuretted hydrogen, but if 8 parts of the glass are fused with one part of potash, the glass produced becomes tarnished on exposure.[2] In a similar manner it has been found by Thorpe and Simmonds[3] that the extent to which lead silicates are attacked by dilute hydrochloric acid depends upon the proportion of acidic to basic oxides present. When there are present in the silicate two or more molecules of acidic oxides to one of basic oxide, dilute acid dissolves out very little lead, whereas when this proportion falls below two, the silicates are readily attacked. Lead silicate forms a constituent of flint glass. The existence of the definite compounds $2PbO,SiO_2$ and PbO,SiO_2 has been proved by various methods of investigation, and the existence of the compound $3PbO,2SiO_2$ is probable.[4]

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[1] Cumming, *Journ. Chem. Soc.*, 1903, 83, 1391.

[2] Faraday, "On the Manufacture of Optical Glass," *Phil. Trans.*, 1830, 120, 1.

[3] *Journ. Chem. Soc.*, 1901, 79, 791.

[4] Hilpert and Weiller, *Ber.*, 1909, 42, 2969; Cooper, Shaw and Loomis, *ibid.*, 3991; Hilpert and Nacken, *ibid.*, 1910, 43, 2565; Cooper, Kraus and Klein, *Amer. Chem. J.*, 1912, 47, 273.

POISONOUS ACTION OF LEAD SALTS.

410 The soluble lead salts are strongly poisonous and are employed in medicine. The normal or basic acetate given in doses containing 1 to 4 grams of lead mostly produces symptoms of acute lead poisoning, whilst 10 grams are said to be a fatal dose.

When taken for a considerable time in small doses, especially in the case of the oxides and carbonates, chronic lead poisoning is observed. The disease called painters' colic is the chronic form of poisoning by carbonate of lead. The symptoms are pain in the abdomen, constipation, loss of appetite, thirst, and general emaciation, followed by a complex of nervous symptoms known as lead-palsy, epileptic fits, and total paralysis.

A very characteristic phenomenon accompanying chronic lead poisoning is the appearance of a blue line at the edges of the gums due to the deposition of lead sulphide. This line is often seen in the case of house-painters and the workmen engaged in white lead works, as well as those occupied in manufactures in which white lead is employed, as, for instance, in the manufacture of glazed cards. Plumbers and others who have to handle metallic lead are also subject to lead poisoning.

A serious source of lead poisoning is the material used by potters for compounding their glazes. This generally consists of litharge, white lead, and red lead, which are readily dissolved by the acids of the gastric juice, and the use of suitable lead silicates has been suggested in place of these substances.[1]

THE ACTION OF WATER UPON LEAD.

411 Since lead acts as a cumulative poison, its salts produce serious results if taken into the system even in very minute quantities for a length of time. Drinking water is often collected in lead-lined cisterns and passes through leaden pipes, and as water in certain circumstances can take up notable quantities of lead it becomes of great importance to determine the conditions under which the solvent action is exerted. A fresh bright surface of lead does not tarnish in a perfectly dry atmosphere, nor when sealed up in a vessel filled with pure distilled water from which all air has been expelled by boiling. If, however, it be exposed to the united action of air and water the lead is oxidised to hydroxide, which dissolves. After a

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[1] Thorpe and Simmonds, *Journ. Chem. Soc.*, 1901, 79, 791.

time, this is converted by the action of the atmospheric carbon dioxide into an insoluble basic carbonate. Lead hydroxide is then again formed, and thus the corrosive action may be continued.[1]

Potable waters always contain a certain amount of salts in solution and the corrosive action on lead depends upon the nature and quantity of the salts thus present. The ammoniacal salts act most prejudicially on water in this respect; this is especially the case with ammonium nitrate, which greatly assists the oxidation and solution of the lead. Other nitrates do not, however, appear to possess this power, and sulphates, phosphates, carbonates, and silicates either retard or altogether prevent this action, and hence water containing carbonic acid in solution or temporarily hard water consisting of a solution of calcium carbonate in carbonic acid gives rise to the formation of insoluble basic lead carbonate;[2] if, however, an excess of carbon dioxide be present, this is dissolved, the water taking up lead in considerable quantity.

The following table (p. 937) contains the results of experiments on the solubility of lead in water containing various salts in solution. Bright plates of lead having a surface of 5,600 sq. mm. were placed in flasks containing 500 c.c. of water in which the salts were dissolved, and the saline solutions allowed to act upon the lead for different periods of time.[3]

Many potable waters act as a solvent of lead, especially waters of a peaty nature which contain organic acids (ulmic and humic acids) and waters containing little or no free carbonic acid, and destitute of calcium and magnesium salts. Occasionally otherwise pure waters are found to contain a trace of free sulphuric acid sufficient to render the water plumbo-solvent and liable to cause lead poisoning.

Epidemics of lead poisoning from such sources have necessitated the treatment of the water by the addition of calcium carbonate (precipitated chalk) alone, if such water contains sufficient free carbonic acid to enable 1·5 grains $CaCO_3$ per gallon to be dissolved, or if the water will not dissolve this amount the addition of from 1 to 5 grains of sodium carbonate (Na_2CO_3) per gallon also.

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[1] See also Thresh, *Analyst*, 1921, 46, 270; Liverseege and Knapp, *J. Soc. Chem. Ind.*, 1920, 39, 27.

[2] See also Antony and Benelli, *Gazz.*, 1896, 26, ii., 97; 1898, 28, ii., 135.

[3] Muir, *Proc. Manch. Phil. Soc.*, 1875, 15, 31; *Journ. Chem. Soc.*, 1877, i., 660. See also Carnelley and Frew, *J. Soc. Chem. Ind.*, 1888, 7, 15, 78; Reichardt, *Arch. Pharm.*, 1887, [3], 25, 858, 1059; Müller, *J. pr. Chem.*, 1887, [2], 36, 317.

Salt.	Grams per litre.	Milligrams per Litre of Lead dissolved.		
		24 hours.	48 hours.	72 hours.
NH_4NO_3	0·02	13·0	—	25·0
"	0·04	15·0	—	32·0
KNO_3	0·02	2·0	2·0	—
$NaNO_3$	0·05			
KNO_3	0·07	—	—	0·5
K_2SO_4	0·50			
KNO_3	0·045	—	—	0·3
K_2CO_3	0·308			
$CaCl_2$	0·25	0·5	0·5	0·5
NH_4NO_3	0·02	—	—	1·8
$CaCl_2$	0·06			
Na_2SO_4	0·02			
K_2CO_3	0·04	—	—	0·1
$CaCl_2$	1·10			
K_2CO_3	0·31	—	—	0·2
Distilled water with carbon dioxide at ordinary pressure		3·0	—	3·0
Ditto with carbon dioxide at a pressure of about 6 atmospheres		14·8	24·0	—
Distilled water		2·0	2·0	3·0

In testing for the presence of lead in water it is important to avoid any form of filtration, inasmuch as lead salts mordant with the filtering paper, and only a small amount of the original soluble lead is found in the filtrate.[1]

DETECTION AND ESTIMATION OF LEAD.

412 The soluble lead salts possess a sweet, astringent taste, whence the name "sugar of lead" has been given to the acetate, and are very poisonous. These two properties of the lead compounds have been long known, and it became in early times of importance to detect the presence of lead, inasmuch as the compounds of this metal were largely employed for a great variety of purposes. Thus, for instance, the Romans were in the habit of boiling their poor wines in leaden vessels, and Pliny mentions

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[1] See, Kolthoff, *Pharm Weekblad*, 1921, 58, 152.

the fact that the point at which the wine becomes sour can be detected by hanging a strip of lead in it and then observing when this undergoes any change in its appearance. In later times the addition of metallic lead to a cask of sour wine was said to render it drinkable. At a still later date, litharge appears to have been employed for the same purpose. It was observed that the treatment of wine with lead could be detected by the addition of sulphuric acid, and in 1707 Zeller suggested that an extract of orpiment and lime water (containing, therefore, sulphide of calcium) was an invaluable test for the presence of lead, inasmuch as this liquid turns all lead salts black. This reaction led to the simultaneous suggestion, in 1787, by Fourcroy and Hahnemann, of the application of water acidified with hydrochloric acid and then saturated with sulphuretted hydrogen for the detection of lead, and thus the most important reagent which we now employ in analytical chemistry for the detection and separation of the metals was introduced.

Potable water may be examined in this way for lead by passing sulphuretted hydrogen through water slightly acidified with hydrochloric acid. It is, however, to be remembered that many other metals, such as mercury, copper, and bismuth, also produce black precipitates. The absence of these metals must, therefore, be ascertained before the presence of lead can be certainly proved. Black lead sulphide can be readily distinguished from other black sulphides insoluble in dilute hydrochloric acid by dissolving it in warm dilute nitric acid and filtering the solution; on addition of sulphuric acid to the filtrate, from which the excess of acid should be removed by evaporation, a white precipitate of lead sulphate is obtained. By means of this reaction lead may be detected in the presence of all the other metals and separated from them.

Lead compounds, heated before the blowpipe on charcoal, yield a malleable bead of lead readily soluble in warm nitric acid, and the solution yields a precipitate with sulphuric acid.

Another characteristic test for lead is, that when present in not too dilute solution, a crystalline precipitate of the chloride is obtained on the addition of hydrochloric acid. This is soluble in boiling water, and separates out on cooling in crystalline needles. Potassium chromate gives, in the presence of free nitric acid, a fine, yellow precipitate of chrome yellow, $PbCrO_4$. In order to detect small quantities of lead in presence of large masses of organic matter, as is necessary in cases of lead poisoning, the mass is evaporated to dryness with sodium carbonate, the residue ignited gently, and the carbonised mass rubbed fine and carefully lixiviated, when small, glittering, heavy spiculæ of metallic lead remain behind. These can be examined as already described.

Lead is easily estimated gravimetrically in the form of sulphate, being precipitated by adding dilute sulphuric acid and then two volumes of absolute alcohol. For certain separations lead is also estimated as the chloride. In this case the solution is precipitated by hydrochloric acid, evaporated on a water-bath, and the concentrated liquid treated with a mixture of ether and alcohol, in which the chloride is insoluble. Lead carbonate and lead oxalate are also occasionally used for the estimation of lead, being converted by ignition into lead oxide.

Volumetrically, lead is determined by the titration of the solution of lead sulphate in ammonium acetate solution with a standard solution of ammonium molybdate, the end point being detected on a spot plate by means of tannin solution.[1]

Lead is also estimated electrolytically. When a solution of lead salt, to which 5 to 7 per cent. of nitric acid has been added, is electrolysed, lead peroxide is deposited at the anode.

Lead compounds impart a pale tint to the non-luminous gas-flame, and this exhibits characteristic lines in the green (Werther). The spark spectrum of lead contains a large number of lines between the orange and violet. The brightest and most characteristic of these are a violet line (4058), a somewhat less bright one in the green (5608), and a fainter one lying near the less refrangible of the "D" lines of Fraunhofer (5875) (Lecoq de Boisbaudran).

The Atomic Weight of lead was determined by Berzelius,[2] by the reduction of pure lead oxide in hydrogen, his results giving the number 207·06; later,[3] during his experimental work on the determination of the atomic weight of sulphur, he converted lead first into nitrate and then into sulphate, and from his results the number 206·96 is obtained. Turner[4] by a similar method obtained 207·04, and Stas[5] 206·92. Baxter and Wilson[6] determined the atomic weight by analyses of lead chloride which had been previously fused in an atmosphere of hydrogen chloride; from the ratio of lead chloride to silver, the number 207·088, and from the ratio to silver chloride, 207·096 was obtained. More recently Baxter and Thorvaldsen[1] have obtained the number 207·19 by analysis of the bromide: while Baxter and Grover[2] found the numbers 207·21 and 207·19 by analysis of the chloride and bromide. The weight of silver necessary to precipitate the halogen from a known weight of lead halide, and the weight of silver halide produced, were both determined. It was shown that lead from non-radioactive sources (" normal " lead) always has the same atomic weight, since the lead used was derived from several different minerals and from sources widely separated geographically. The mean of these last numbers, 207·20, is now (1922) adopted as the atomic weight of lead, though later determinations, having as their object the comparison of the atomic weights of normal lead with that of lead from radioactive sources, rather than the absolute value of the atomic weight, indicate a slightly lower number. By analysis of the chloride, Honigschmid and Horowitz[3] obtain the number 207·18; Richards and Lembert[4] 207·15: Richards and Wadsworth[5] 207·18: and Richards and Hall[6] 207·19.

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[1] See also Sasse, *Pharm. Zeit.*, 1920, **65**, 559, 668; Kolthoff, *Pharm. Weekblad*, 1920, **57**, 934; Simmons, Gordon, and Boehmer, *Canad. Chem. J.*, 1920, **4**, 139.

[2] *Lehrbuch*, **3**, 1218.

[3] *Ibid.*, 5th ed., **3**, 1187.

[4] *Phil. Trans.*, 1833, **123**, 527.

[5] *Bull. Acad. roy. Belg.*, 1860, [2], **10**, 208.

[6] *J. Amer. Chem. Soc.*, 1907, **30**, 187.

ISOTOPES OF LEAD.

413 The study of radioactivity leads to the belief that there are nine isotopes (*q.v.*) of lead; of these, the final disintegration product of uranium (238), by loss of eight α-particles, should be lead of atomic weight 206; while the final product of thorium (232), by the loss of six α-particles, should be lead of atomic weight 208.

Confirmation of this was first obtained by Soddy and Hyman,[7] who found lead derived from thorite, a radioactive mineral from Ceylon consisting chiefly of hydrated thorium silicate, has an atomic weight of 208·4. It has since been amply confirmed that lead from a radioactive source in which thorium predominates has a higher atomic weight than normal lead, though the number 208·4 is probably too high. Honigschmid[8] obtained the number 207·90 for lead from Norwegian thorite. Richards and his collaborators, and Honigschmid, have shown that lead derived from a radioactive source in which uranium predominates has a lower atomic weight than normal lead; the lowest value yet obtained, 206·05, is for lead from a crystallised uranium mineral from Morogoro in Tanganyika territory.

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[1] *J. Amer. Chem. Soc.*, 1915, **37**, 1021.

[2] *Ibid.*, 1915, **37**, 1027.

[3] *Monatsh.*, 1915, **36**, 355.

[4] *J. Amer. Chem. Soc.*, 1914, **36**, 1329.

[5] *Ibid.*, 1916, **38**, 227 and 2013.

[6] *Ibid.*, 1917, **39**, 537.

[7] *Journ. Chem. Soc.*, 1914, **105**, 1402.

[8] *Zeit. Elektrochem.*, 1919, **25**, 91.

It has been shown that different isotopes have the same melting point within the limits of experimental error;[1] that their atomic volumes are the same, for their densities are proportional to their atomic weights;[2] that the solubilities of their nitrates are the same, if the results are expressed in moles per litre,[3] that they cannot be separated by fractional crystallisation of their nitrates; and that the refractive indices for sodium light of their nitrates are the same. Only a slight difference in the position of one line in the spectra of different isotopes was detected by Soddy and Hyman, and has been confirmed by Merton.[4]

A possible partial separation of the isotopes of lead by a chemical method has been described;[5] but the results require confirmation.

The lead content of radioactive minerals is regarded as a valuable indication of their age. Since there is no evidence that all the lead present in a mineral is derived from radioactive disintegration, the lead content can only give an upper limit to its age.[6]

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[1] Richards and Hall, *J. Amer. Chem. Soc.*, 1920, **42**, 1550; Lembert, *Zeit. Elektrochem.*, 1920, **26**, 59.

[2] Soddy, *Nature*, 1921, **107**, 41.

[3] Richards and Schumb, *J. Amer. Chem. Soc.*, 1918, **40**, 1403.

[4] *Proc. Roy. Soc.*, 1920, **96**, [*A*], 388; 1921, **100**, [*A*], 84.

[5] Dillon, Clarke, and Hinchy, *Sci. Proc. Roy. Dublin Soc.*, 1922, **17**, 53.

[6] Lawson, *Sitzungsber. Akad. Wiss. Wien*, 1917, **126**, 2A, 721.

GROUP V.

Sub-group (*a*).	*Sub-group* (*b*).
Nitrogen.	Phosphorus.
Vanadium.	Arsenic.
Columbium (Niobium).	Antimony.
Tantalum.	Bismuth.

413 As in the preceding group (p. 831), the members of the two sub-groups resemble one another, especially in chemical properties, very closely, although they differ in certain respects.

All the elements of the group are characterised by the existence of acid-forming oxides of the empirical formula R_2O_5, the acidity of the resulting acid diminishing as the atomic weight of the element rises. Thus it is doubtful whether any salts of bismuthic acid exist, whereas the vanadates, arsenates, etc., are well-defined and stable salts.

The elements vanadium, columbium, and tantalum, which, with nitrogen, belong to the even series, combine so readily with oxygen that it is difficult to obtain them pure. They all have a metallic appearance, and melt and boil only at very high temperatures. They do not form volatile compounds with hydrogen or the alcohol radicles.

The elements of the odd series, phosphorus, arsenic, antimony, and bismuth, on the other hand, are easily reduced from their oxides, melt at moderate temperatures, and can all readily be volatilised. They exhibit in their external characteristics the gradual passage from a well-marked non-metallic element (phosphorus) to a well-defined metal (bismuth), and the same progression is to be traced also in their chemical properties. Thus the lower oxide of phosphorus, of the empirical formula P_2O_3, is the anhydride of a well-marked acid, but does not yield salts, even with strong acids. Arsenious oxide yields unstable salts with strong acids, such as sulphuric acid; the corresponding oxide of antimony yields more stable salts, and the trioxide of bismuth is entirely devoid of acid-forming properties, and reacts with acids to form a whole series of salts of the type RX^I_3.

The same increase in basicity is observable in the sulphides of these elements, as well as in the pentoxides.

Phosphorus, arsenic, and antimony, as well as nitrogen, yield very characteristic volatile hydrogen compounds; a hydride of bismuth has also been prepared. They all form organometallic derivatives.

The group is further characterised by the large number of oxides and halogen derivatives formed by its members. In many of these the valency of the elements varies considerably. They are all distinguished by a tendency to form two series of compounds of the types RX^{I}_3 and RX^{I}_5 (or $R_2X^{II}_3$, $R_2X^{II}_5$), but, in addition to this, some of them act also as dyads and tetrads. Thus nitrogen is divalent in nitric oxide, NO, and tetravalent in nitrogen peroxide, NO_2, whilst vanadium forms a dichloride, VCl_2, and a tetrachloride, VCl_4.

The elements nitrogen, phosphorus, and arsenic, and their chief derivatives, have already been described in Vol. I.

THE VANADIUM GROUP.

VANADIUM. V = 51·0. At. No. 23.

414 In 1801, Del Rio pointed out the existence of a new metal in a lead ore found at Zimapan, in Mexico,[1] and gave to it the name erythronium, from the fact that its salts became red when heated with acids. In 1805, Collet-Descotils[2] expressed his opinion that this supposed new metal was an impure oxide of chromium, and Del Rio accepted this conclusion as correct. In 1830, Sefström[3] described a new metal which he found in the celebrated iron of Taberg, and for this he proposed the name of Vanadium, from *Vanadis*, a cognomen of the Scandinavian goddess Freia. In the same year Wöhler[4] showed that Del Rio's discovery was a true one, and that the Zimapan ore was a vanadate of lead. Unable to carry out the further investigation of the new metal, Sefström handed the materials, amounting only to a few grams, to Berzelius, and in 1831 this chemist[5] published the result of an exhaustive investigation on the subject, in which he described a large number of vanadium compounds, and came to the conclusion that vanadium

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[1] *Gilbert's Ann.*, 1801, 71, 7.

[2] *Ann. Chim. Phys.*, 1805, [1], 53, 260.

[3] *Pogg. Ann.*, 1830, 21, 43.

[4] *Ibid.*, 1831, 22, 1.

[5] *Ibid.*

closely resembled chromium and molybdenum, yielding, like these metals, an acid-forming trioxide. This view was universally adopted until the year 1867, when Roscoe showed that the substance supposed by Berzelius to be vanadium was, according to the mode of its preparation, either an oxide or a nitride; that the volatile trichloride of Berzelius contained oxygen and possessed a composition analogous to that of phosphorus oxychloride; and that the metal, instead of belonging, as was supposed, to the chromium group, was a member of the antimony group and intimately connected with the nitrogen, phosphorus, and arsenic family.[1]

415 Vanadium is a somewhat rare substance, forming an essential constituent of only comparatively few scarce minerals. Traces of this element are, however, tolerably widely distributed throughout terrestrial matter; it is found in meteorites of the stony type,[2] and it exists in the sun.

The principal vanadium minerals are vanadinite, or lead vanadate, $3Pb_3(VO_4)_2,PbCl_2$; dechenite, $(Pb,Zn)(VO_3)_2$; descloizite, $Pb_2V_2O_7$; pucherite, $BiVO_4$; psittacinite,

$$(Pb,Cu)_3(VO_4)_2,3Cu(OH)_2,6H_2O;$$

volborthite, $(Cu,Ca)_3(VO_4)_2,H_2O$; roscoelite (vanadium mica), a vanadium muscovite, containing the metal as the basic oxide,[3] V_2O_3; mottramite, $(Pb,Cu)_3(VO_4)_2,2(Pb,Cu)(OH)_2$; sulvanite, $3Cu_2S,V_2S_5$; carnotite, a potassium uranium vanadate found in Colorado; and patronite, an impure sulphide of vanadium, which occurs in considerable quantity in Peru. Mottramite has been found in tolerable quantity in the copper-bearing beds of the keuper, worked at Alderley Edge and Mottram St. Andrews in Cheshire, and it is from this source that the vanadic acid of commerce was at one time obtained. Small amounts of vanadium have also been found in a large number of clays, in trap and basalt,[4] in certain iron ores, especially magnetite,[5] and cast-iron, in larger quantities in the slag from the basic steel process at Creuzot, in rutile, in the ash of trees, in certain coals, lignites, and peats, and also in soda-ash, as well as in sodium phosphate.

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[1] A bibliography has been compiled by Prandtl (Liepsig, 1906, Voss). More complete information concerning the compounds of vanadium may be obtained from the monograph by Ephraim (Stuttgart, Enke, 1904).

[2] Hasselberg, *K. Vet. Akad. Förh. Stockholm*, 1899, 56, 131.

[3] Hillebrand, Turner and Clarke, *Amer. J. Sci.*, 1899, [4], 7, 451. It occurs in fairly large quantities associated with gold and gold tellurides in Eldorado Co. in California; also in Colorado and at Kalgoorlie in Western Australia.

[4] See Hillebrand, *Amer. J. Sci.*, 1898, [4], 6, 209; 7, 294.

[5] See Pope, *Journ. Chem. Soc.*, 1900, 78, ii., 409.

Extraction and Preparation of Vanadium Compounds.—In order to prepare vanadium salts from mottramite, the keuper-sandstone, which contains the mineral deposited as a film on the surface of the grains of sand, is digested with strong hydrochloric acid, the acid liquor drawn off, and the sand well washed with water. The acid solution, together with the washings, is evaporated down with an excess of ammonium chloride, when ammonium metavanadate separates out, and this is repeatedly crystallised to free it from copper and iron. The crude ammonium metavanadate is then gently roasted in porcelain, by which means the vanadium pentoxide is obtained in a tolerably pure condition. In order to purify this it is suspended in water and ammonia gas passed into the liquid. A solution of ammonium vanadate is thus formed, which is separated by filtration from the residue containing silica, phosphates, etc., and then crystallised by evaporation in platinum vessels; the pentoxide obtained by several repetitions of this treatment is free from phosphorus.

Vanadic acid may be prepared in a similar manner from *carnotite*, which is an important mineral commercially, being a source of uranium and radium. It is preferable, however, to boil the mineral with an excess of sodium carbonate, when practically all the uranium and about two-thirds of the vanadium pass into solution as sodium uranate and vanadate, and the radioactive matter remains in the residue. By filtering the solution and concentrating until it is saturated with sodium carbonate, most of the uranium separates out as a yellow double salt, $UO_2CO_3,2Na_2CO_3$, and on cooling the hot filtrate from this salt much of the excess of sodium carbonate crystallises out. The filtrate then contains sodium vanadate together with excess of sodium carbonate and a little uranium, which may be precipitated as sodium diuranate, $Na_2U_2O_7,6H_2O$, by addition of caustic soda.[1]

416 *Metallic Vanadium.*—Berzelius obtained brilliant metallic scales by heating the oxytrichloride in an atmosphere of ammonia. These do not, however, consist of metallic vanadium, but of vanadium nitride. Pure metallic vanadium was first obtained by the reduction of the dichloride in perfectly pure hydrogen. Although this process appears simple enough, there is no metal more difficult to prepare in this way than vanadium. This

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[1] See Plum, *J. Amer. Chem. Soc.*, 1915, **37**, 1797.

arises from the fact that whilst vanadium is stable at the ordinary atmospheric temperatures, it absorbs oxygen at a red heat with the greatest avidity, so that every trace of air or moisture must be excluded during its preparation. Moreover, the dichloride itself cannot be readily obtained in quantity.

Roscoe's apparatus is shown in Fig. 189. The hydrogen generator (A) yields a stream of hydrogen which can be kept constantly passing through the wash-bottles for a week at a time, by occasionally adding fresh acid to the upper bottle and drawing off the zinc sulphate solution from the lower bottle. The first wash-bottle contains a solution of lead acetate, the second one of silver nitrate, and the three others contain boiled sulphuric acid. Traces of oxygen arising either from diffusion or from air absorbed in the dilute acid used are removed in the tube (CD) attached to the last washing-bottle; the first portion of the tube contains red hot platinum sponge (C), whilst the further portion of the tube (D) is filled with phosphorus pentoxide and plugs of cotton-wool. The greatest care must be taken to have all rubber stoppers and joints made as tight as possible with copper-wire and paraffin. At right angles to the drying tube (CD) is placed the reducing arrangement shown in the lower part of the drawing. This consists of a porcelain tube (EE′) placed in a Hofmann's furnace and protected in the central portions, where it is heated by an outer casing of sheet-iron. The porcelain tube is connected with the hydrogen apparatus by means of the wide glass tube (FF′) provided with the tubulus (G) and narrowed down to join the drying tube at F′. The joint between the porcelain and glass tubes is made of seamless rubber, well wired and covered by an outer short glass cylinder, the space between the tubes and the cylinder being filled either with mercury or fused paraffin, and a similar joint is placed at the further end of the porcelain tube.

The dichloride is contained in the bent tube (H) in which it was prepared and sealed up in hydrogen. It is fitted through the tubulus (G). The platinum boat being in position, as shown in the figure, hydrogen is allowed to pass through the apparatus for twelve hours to dry it completely and clear out the air; the rubber stopper of the tubulus is then withdrawn and the end of the tube containing the dichloride cut off, and the tube and stopper are quickly replaced, so that the crystals lie in the horizontal portion of the tube, which is then so turned in the stopper that the crystals of dichloride fall into the platinum boat below. This boat, charged with dichloride, is then drawn into the centre of the porcelain tube by means of the platinum wire, the end of which (w) passes tightly through a small hole

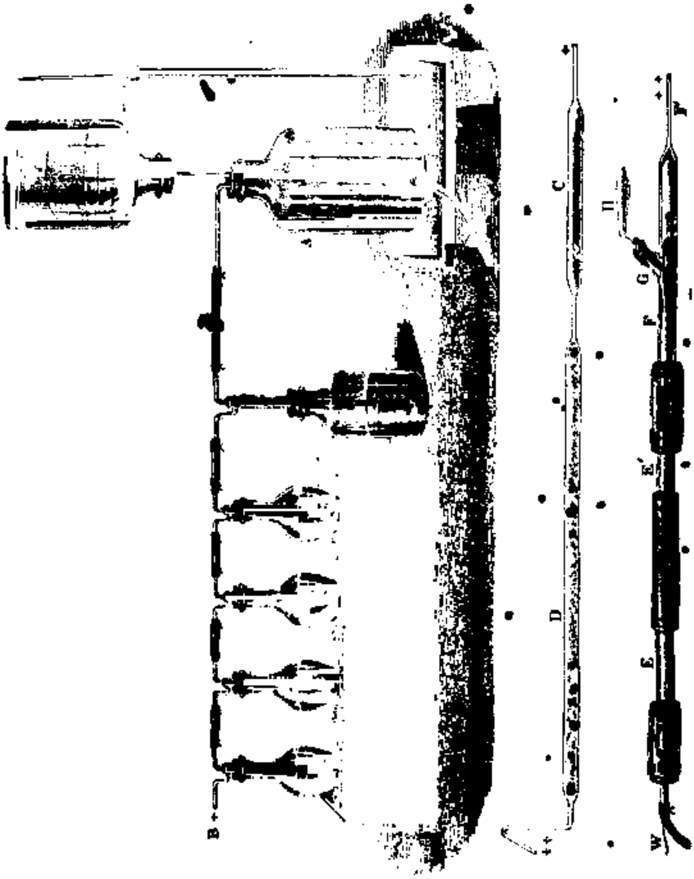

FIG. 169.

in the rubber tube at the end of the apparatus; the wire is then cut off short at the end of the glass tube, a proper joint made, and an exit tube attached dipping under sulphuric acid.

The rubber stopper of the tubulus is surrounded by a bath of paraffin and the hydrogen is allowed to bubble through for six hours. The porcelain tube is then gradually raised to the highest temperature (a bright red heat) the Hofmann's furnace will yield, and kept constant until some hours after the last trace of hydrogen chloride can be detected in the issuing hydrogen. The process lasts from forty to eighty hours, according as the quantity of dichloride employed varies from 1 to 3 or 4 grams.

Reduction of vanadium pentoxide with carbon in the electric furnace yields only an impure metal, containing a large amount of carbon.[1] Pure vanadium can be prepared by reducing the pentoxide with a mixture of the metals of the rare earths, known as "mischmetall," obtained by the reduction of the waste oxides from the manufacture of thoria.[2] The oxide is mixed with the finely divided metal in a magnesia crucible and the mass ignited, as in the aluminium thermite process; a violent reaction occurs and a regulus of pure vanadium is produced. The metal has been prepared also by passing the electric current through thin rods of V_2O_3 contained in a vacuum,[3] by heating the trioxide and carbide in a zirconia crucible to 1950°,[4] and by passing the vapour of vanadium chloride over heated sodium hydride.[5] A regulus of crude vanadium, probably consisting of a mixture of the metal and the dioxide, can be obtained from vanadic oxide by Goldschmidt's aluminium reduction method. It can be used for the preparation of the tetrachloride.[6]

Metallic vanadium prepared by reduction from the dichloride in hydrogen, is a light whitish-grey coloured powder, which under the microscope reflects light most powerfully, and appears as a brilliant crystalline, metallic mass possessing a silver-white lustre. The surface of a regulus of the metal is covered with twinned rhombohedral crystals, and the metal has a hardness greater than that of steel or quartz. It is of a brilliant silver-white colour and takes a splendid polish which is not affected by air. Vanadium does not decompose water at the ordinary temperature and is neither volatile nor fusible when heated to redness in hydrogen. When the powdered metal is thrown into a flame, or rapidly heated in an excess of oxygen, it burns with brilliant scintillations. The specific gravity of vanadium at 15° is 5·5, and the atomic heat, as deduced from the specific heat of its alloys, is normal.[1] The metal is not attacked by hydrochloric acid either when cold or hot, and neither strong nor dilute sulphuric acid acts upon it in the cold, but when heated with the strong acid it slowly dissolves, giving a greenish-yellow solution. Hydrofluoric acid dissolves the metal slowly with evolution of hydrogen and formation of a green solution, whilst nitric acid of all strengths oxidises it with violence, evolving nitrous fumes and forming a blue liquid. Vanadium also dissolves readily in chloric acid, perchloric acid, and ammonium persulphate, vanadic acid being produced.[2] Both hot and cold solutions of caustic soda are without action on the metal, but when fused with the hydroxide, hydrogen is evolved and a vanadate formed. Metallic vanadium precipitates platinum, gold, and silver from solutions of their salts, and reduces mercuric, cupric, and ferric salts to the corresponding lower salts (Marino). When heated in an atmosphere of pure nitrogen, it is converted into the mononitride (Roscoe).

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[1] Moissan, *Compt. rend.*, 1893, **116**, 1225.

[2] Weiss and Aichel, *Annalen*, 1904, **337**, 380.

[3] Werner von Bolton, *Zeit. Elektrochem.*, 1905, **11**, 45.

[4] Ruff and Martin, *Zeit. angew. Chem.*, 1912, **25**, 49.

[5] Billy, *Compt. rend.*, 1914, **158**, 578.

[6] Koppel and Kaufmann, *Zeit. anorg. Chem.*, 1905, **45**, 352.

Alloys of vanadium can be prepared in the electric furnace by reducing vanadic anhydride in the presence of the second metal or one of its oxides.[3] It also forms an alloy with platinum. Ferrovanadium is manufactured on a commercial scale in the electric furnace in France and also in Colorado. It is used in the production of vanadium steel (see Steel).

COMPOUNDS OF VANADIUM.

VANADIUM AND OXYGEN.

417 Vanadium forms five compounds with oxygen, analogous to the oxides of nitrogen, namely:

Vanadium suboxide	V_2O.
Vanadium monoxide, hypovanadious oxide	VO or V_2O_2.
Vanadium sesquioxide, vanadium trioxide .	V_2O_3.
Vanadium dioxide, hypovanadic oxide .	VO_2 or V_2O_4.
Vanadic anhydride, vanadium pentoxide .	V_2O_5.

All these oxides form salts, the three first acting only as basic oxides, the two highest both as acid-forming oxides and as weak basic oxides.

Some confusion exists as to the nomenclature of the various oxides of vanadium and the series of compounds derived from them. Roscoe, to mark the analogy with arsenic and phosphorus, termed the sesquioxide, V_2O_3, vanadious oxide, and its salts the vanadious salts, and to the lower oxide, VO or V_2O_2, he gave the name hypovanadious oxide. The fact that V_2O_3 acts entirely as a basic oxide, and the close analogy existing between the derivatives of V_2O_3 and of VO and the corresponding chromium compounds, have led more recent investigators[1] to term the compounds derived from V_2O_3 the vanadic salts, and those derived from VO the vanadious salts, corresponding with the chromic and chromous salts respectively. The salts formed by the oxide VO_2 with bases, termed by Roscoe hypovanadates, are now usually called vanadites, and the salts with acids containing the divalent radicle VO (or the tetravalent radical V_2O_2) are known as vanadyl (or divanadyl) compounds. The more modern nomenclature has been adopted here.

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[1] Matignon and Monnet, *Compt. rend.*, 1902, **134**, 542.

[2] Marino, *Zeit. anorg. Chem.*, 1904, **39**, 152.

[3] Moissan, *Compt. rend.*, 1896, **122**, 1297.

418 *Vanadic Anhydride*, V_2O_5.—The preparation of this oxide from mottramite has already been described. In the pure state it is best prepared by decomposing the oxytrichloride, $VOCl_3$, with water and fusing the residue, but it can also be obtained pure by heating pure ammonium metavanadate and avoiding any reduction.[2] Vanadic anhydride crystallises in splendid yellowish-red, rhombic prisms (Nordenskiöld), which have a specific gravity of 3·35 (J. J. Watts), and dissolve in about 1,000 times their weight of water, giving a yellowish solution, which does not possess any taste but turns blue litmus paper red. Vanadic anhydride fuses without decomposition in absence of organic reducing matter to a red liquid, which on cooling yields brilliant, transparent, reddish-yellow needles, and at the moment of crystallisation exhibits the phenomenon of incandescence.

Vanadic anhydride exists in several different modifications, which differ in solubility and other properties. When it is prepared by igniting ammonium vanadate, evaporating with nitric acid, and gently heating the residue, it forms a yellow, hygroscopic powder, which unites with water to form hydrates containing 1, 2, and 8 molecules of water, and dissolves in cold water to the extent of 8 grams per litre. When the oxide is heated for a long time at 440° or fused, it is converted into two different sparingly soluble modifications.[3]

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[1] Piccini and Marino, *Zeit. anorg. Chem.*, 1902, **32**, 57.

[2] Matignon, *Chem. Zeit.*, 1905, **29**, 986.

[3] Ditte, *Compt. rend.*, 1885, **101**, 698.

Vanadic anhydride acts as a weak basic oxide as well as an acid-forming oxide. Thus it dissolves in strong acids, forming red or yellow solutions yielding crystalline compounds, which separate out on spontaneous evaporation or cooling.

Vanadic anhydride is reduced by sulphurous acid in presence of sulphuric acid, and by evaporation with hydrochloric acid, to VO_2; magnesium and hydrochloric acid, or evaporation with hydriodic acid, reduce it to V_2O_3, whilst zinc and hydrochloric acid carry the reduction to VO.

Vanadic anhydride has been used in the preparation of aniline black, and its use has been suggested in the electrolytic oxidation and reduction of various organic compounds in an acid bath, *e.g.*, the manufacture of quinone from aniline, etc.[1] It also greatly accelerates certain oxidation processes, such as the action of nitric acid on sugar, the oxidation of alcohol by atmospheric oxygen, etc.[2]

THE VANADIC ACIDS AND THEIR SALTS.

419 *Normal Vanadic Acid*, H_3VO_4, is not known.

Metavanadic Acid, HVO_3, was discovered by Gerland.[3] It forms a fine yellow pigment, sometimes termed vanadium bronze, and is employed in place of gold bronze. It is obtained in the form of brilliant scales of a golden or orange colour by boiling aqueous sulphurous acid with copper vanadate, prepared by the double decomposition of ammonium metavanadate and copper sulphate. A mixture of brown and orange-yellow crystals is obtained, and on continuing the ebullition with more sulphurous acid, the brown crystals dissolve, the yellow metavanadic acid being insoluble.

Vanadium bronze may also be prepared by adding a solution of ammonium vanadate to one of copper sulphate containing excess of ammonium chloride until a permanent precipitate is formed, and then gently heating to 75°, when the yellow scales are slowly deposited, and after the lapse of a few hours nearly the whole of the vanadium is precipitated. The larger the quantity of material employed and the slower the action takes place, the finer is the colour of the bronze.[4]

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[1] German Patent, 172654 (15/9/03).

[2] Moser and Lindenbaum, *J. pr. Chem.*, 1907, [2], 75, 146; German Patent, 183022 (18/8/05).

[3] *Proc. Manch. Phil. Soc.*, 1873, 12, 50.

[4] *Ber.*, 1876, 9, 874.

If the freshly prepared solution of copper vanadate be quickly evaporated in a flat dish, a crystalline residue is obtained which is soluble in water, and when this solution is dialysed for some days a clear solution of pure vanadic acid is obtained which remains clear when heated, and deposits the red amorphous pentoxide on evaporation.

A solution of vanadic acid is decomposed on heating with sulphuric acid.[1]

Pyrovanadic Acid, $H_4V_2O_7$, is a brown precipitate closely resembling ferric hydroxide, obtained by treating a solution of an acid vanadate with nitric acid. When air-dried it possesses the above composition. It is, however, unstable and loses half its water when dried over sulphuric acid (v. Hauer).

Hexavanadic Acid, $H_4V_6O_{17} = 6V_2O_5,2H_2O$.—When a solution of pervanadic acid is allowed to stand it loses oxygen and forms an acid yellow liquid, which probably contains hexavanadic acid. The solution is unstable and soon deposits a brown precipitate of vanadium pentoxide.[2]

The Vanadates.—The so-called normal vanadates prepared by Berzelius correspond to the metaphosphates; it is also possible to prepare ortho- and pyro-vanadates analogous to the corresponding phosphates. v. Hauer's so-called di- and tri-vanadates[3] are most simply formulated as tetra- and hexa-vanadates, $Na_2V_4O_{11}$ and $Na_2V_6O_{16}$, but it is probable from the researches of Düllberg on the molecular weights and conductivities of these salts that they are in reality acid salts derived from hexavanadic acid, $H_4V_6O_{17}$, the normal salt of which, $Na_4V_6O_{17}$, is also known. Thus we have:

(1) Sodium Metavanadate	$NaVO_3$.
(2) Sodium Orthovanadate	Na_3VO_4.
(3) Sodium Pyrovanadate	$Na_4V_2O_7$.
(4) Sodium Tetravanadate (v. Hauer)	$Na_3HV_6O_{17}$.
(5) Sodium Hexavanadate „	$Na_2H_2V_6O_{17}$.

Other more complicated polyvanadates are known.[4]

The order of stability of the soluble vanadates in aqueous solution differs remarkably from that of the phosphates, the metavanadates being the most stable and the orthovanadates the least stable, whereas in the phosphorus series the order of stability is the reverse of this. At a high temperature, on the other hand, the orthovanadate is the most stable, being formed when vanadium pentoxide is fused with an alkali carbonate, the meta-salt being produced when a solution of an alkali carbonate is boiled with vanadium pentoxide.

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[1] Auger, *Compt. rend.*, 1921, **173**, 306.

[2] Düllberg, *Zeit. physikal. Chem.*, 1903, **45**, 170.

[3] *J. pr. Chem.*, 1856, **69**, 385; 1859, **76**, 156, 929; 1860, **80**, 324.

[4] Carnelley, *Journ. Chem. Soc.*, 1873, **26**, 323; Rosenheim, *Zeit. anorg. Chem.*, 1916, **96**, 139; *ibid.*, **96**, 223.

The property which serves best to distinguish the ortho- from the meta-vanadates is the colour of the respective copper salts. Copper orthovanadate possesses a blue-green colour, whilst the metavanadate is a light yellow, crystalline powder.

The alkali pyrovanadates are soluble, and can be readily obtained by fusing one molecule of vanadium pentoxide with two molecules of the carbonate of an alkali metal, dissolving, and crystallising. They are likewise obtained by the decomposition of an aqueous solution of the corresponding orthovanadate. The pyrovanadates of the heavy metals are usually insoluble in water, and possess properties generally similar to those of the corresponding orthovanadates.

The metavanadates are usually yellow: some of them, especially those of the alkaline earths, zinc, cadmium, and lead, are converted into colourless isomeric modifications, in the solid state under water, in aqueous solution, and especially in the presence of alkali carbonates. The metavanadates of the alkali metals are colourless, and on treatment with an acid give rise to anhydro-salts, which have a fine yellowish-red colour. The metavanadates of ammonium, potassium, sodium, barium, and lead are but sparingly soluble in water. The other metavanadates are more soluble. It is probable that sodium metavanadate has the molecular formula $Na_3V_3O_9$, thus corresponding with the trimetaphosphate (Düllberg). The following are the properties of the most important members of these three classes of vanadates.

Potassium Metavanadate, KVO_3, dissolves slowly in cold and readily in hot water, and with difficulty in caustic potash. When it is boiled with water and vanadium pentoxide, or fused with the latter, *potassium tetravanadate*, $K_2V_4O_{11},3H_2O$, or $K_3HV_6O_{17},4H_2O$ (Düllberg), is obtained, crystallising in broad, reddish-yellow tablets. This salt is slightly soluble in cold and very easily soluble in hot water.

Sodium Orthovanadate, Na_3VO_4.—This salt crystallises with 16, 12, 10, and $8H_2O$, and in the form with $12H_2O$ is isomorphous with sodium orthophosphate. It has a strongly alkaline reaction, and in aqueous solution is completely hydrolysed to caustic soda and sodium pyrovanadate:

$$2Na_3VO_4 + H_2O = Na_4V_2O_7 + 2NaOH.$$

Sodium Pyrovanadate, $Na_4V_2O_7,18H_2O$, crystallises in large, six-sided tablets, is easily soluble in water, and is precipitated by alcohol from its aqueous solution in pearly scales. It fuses more easily than the orthovanadate, and is first formed in the preparation of the latter salt.

Sodium Metavanadate, $NaVO_3$, resembles the potassium salt, and is converted in a similar manner into *sodium tetravanadate*, $Na_2V_4O_{11},9H_2O$, or $Na_3HV_6O_{17},13H_2O$ (Düllberg), which separates out in beautiful large orange-red crystals. This salt is only slightly soluble in water, but possesses such powerful colouring properties that 1 part of it is sufficient to impart a yellow tint to 200,000 parts of water. It effloresces on exposure to the air, becoming of a reddish-brown tint, and melts at a dark red heat, solidifying to a dark red, amorphous mass.

Ammonium Metavanadate, NH_4VO_3, is the most important vanadate. It is obtained by dissolving the pentoxide in an excess of ammonia and evaporating, or by precipitating with alcohol, in which it is insoluble. It forms colourless, transparent, crystalline crusts, and is insoluble in concentrated solution of ammonium chloride, and accordingly is precipitated when a lump of ammonium chloride is allowed to remain in a solution of a metavanadate or pyrovanadate:

$$Na_4V_2O_7 + 4NH_4Cl = 2NH_4VO_3 + 2NH_3 + H_2O + 4NaCl.$$

The solution of this salt becomes of a deep black tint when treated with tincture of galls, and Berzelius originally suggested the use of this liquid as an ink. This ink is, however, not permanent, "for letters thus written by Berzelius are now quite illegible." (Wöhler). It was once used in dyeing with aniline black, since its presence greatly facilitates the oxidation of the aniline hydrochloride on which the formation of the colouring matter depends.

Ammonium Tetravanadate, $(NH_4)_2V_4O_{11},4H_2O$, or
$(NH_4)_3HV_6O_{17},5\frac{1}{2}H_2O$,
is obtained by the addition of acetic acid to a boiling solution of the metavanadate until the precipitate redissolves. The salt separates out from the yellowish-red liquid on cooling in large,

transparent, orange-red crystals. If it be recrystallised from water containing acetic acid, splendid red crystals of *ammonium hexavanadate*, $(NH_4)_2V_6O_{16},6H_2O$ or $(NH_4)_2H_2V_6O_{17},5H_2O$ are obtained.

Calcium Pyrovanadate, $2Ca_2V_2O_7,5H_2O$, is a white, amorphous precipitate obtained by double decomposition of the corresponding sodium salt with calcium chloride. If the solution of sodium orthovanadate be precipitated by calcium chloride, the same salt is obtained mixed with calcium hydroxide, the orthovanadate being at once decomposed according to the equation:

$$Ca_3(VO_4)_2 + H_2O = Ca_2V_2O_7 + Ca(OH)_2.$$

Lead Orthovanadate, $Pb_3(VO_4)_2$, is a nearly white, insoluble precipitate obtained by adding a solution of lead acetate to one of sodium orthovanadate. This salt occurs in nature combined with lead chloride as vanadinite, $3Pb_3(VO_4)_2,PbCl_2$ or $Pb_3(VO_4)_2,Pb_2(VO_4)Cl$. This mineral crystallises in hexagonal prisms, having a reddish-brown colour, and is isomorphous with apatite. It has a specific gravity of from 6·6 to 7·2, and frequently contains some phosphoric acid. It was found by Del Rio in Zimapan in Mexico, and occurs also at Leadhills in Scotland, in Carinthia, and in the Urals. It may be obtained artificially by fusing together lead oxide, vanadium pentoxide, and lead chloride, in the right proportions. The fused mass contains druses, in which thin, needle-shaped crystals are contained. If boiled with water it falls to a crystalline powder consisting of microscopic, hexagonal prisms, possessing the waxy lustre and the yellowish colour of natural vanadinite, and having a specific gravity of 6·7 (Roscoe).

Lead Pyrovanadate, $Pb_2V_2O_7$, is found in South America as descloizite in rhombic crystals, which have an orange-green or black colour, a bronze lustre, and a specific gravity of 5·839. It usually contains zinc, iron, manganese, and copper as impurities. If a solution of sodium pyrovanadate be precipitated with lead acetate, the basic salt, $Pb_4V_4O_{15}$, is thrown down as a light-yellow precipitate.

Lead Metavanadate, $(Pb(VO_3)_2$, is obtained as a yellow precipitate when a solution of a metavanadate is mixed with one of lead acetate. The mineral dechenite consists chiefly of this compound, a portion of the lead, however, being usually replaced by zinc. It occurs together with lead ores, forming yellow, brown, or deep-red reniform masses, having a specific gravity of 5·6 to 5·8.

Lead Tetravanadate, $Pb_2V_4O_{11}$, is obtained by precipitating the corresponding potassium salt with lead nitrate in the form of a reddish-yellow precipitate slightly soluble in water.

Copper Orthovanadate, $Cu_3(VO_4)_2,H_2O$, occurs as the mineral volborthite, in which a part of the copper is replaced by calcium; it crystallises in small yellow or green hexagonal tablets having a specific gravity of 3·55, and is found in Thuringia and in the Urals. *Copper Pyrovanadate*, $Cu_2V_2O_7$, is a yellow, crystalline precipitate, whilst *copper metavanadate* is an apple-green precipitate.

Silver Orthovanadate, Ag_3VO_4, is obtained by precipitating a freshly prepared solution of the sodium salt with silver nitrate. It is a deep orange-red coloured precipitate, which is easily soluble in nitric acid and in ammonia.

Silver Pyrovanadate, $Ag_4V_2O_7$, is a heavy, yellow powder.

Silver Metavanadate, $AgVO_3$, forms a pale yellow, gelatinous precipitate.

Vanadic acid, like phosphoric acid, yields complex compounds with stannates,[1] tungstates, and molybdates, as well as with phosphates and arsenates.[2]

Pervanadic Acid and the Pervanadates.—The alkali metavanadates are readily converted by hydrogen peroxide into per-salts of the formula $R'VO_4$, many of which have been prepared pure. They are decomposed by dilute acids with evolution of one atomic proportion of oxygen.[3]

Pervanadic Acid, HVO_4, is formed when vanadium pentoxide is added to hydrogen peroxide in dilute sulphuric acid solution. A deep-red coloured liquid is formed,[4] which deposits unstable yellow crystals of the per-acid.[5]

Potassium Pervanadate, KVO_4, is a yellow, microcrystalline precipitate, obtained by dissolving potassium metavanadate in a solution of hydrogen peroxide containing sulphuric acid, and precipitating with alcohol.

Barium Metapervanadate, $Ba(VO_4)_2$, is obtained as an amorphous, yellow precipitate, when a solution of barium chloride is added to a saturated solution of ammonium metavanadate in 30 per cent. hydrogen peroxide. Other salts have been prepared in a similar manner; they are characterised by being bright yellow or deep orange.

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[1] Prandtl, *Ber.*, 1907, 40, 2125.

[2] For an account of these complex derivatives, see the monograph by Ephraim quoted on p. 944.

[3] Scheuer, *Zeit. anorg. Chem.*, 1898, 16, 284; Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1902, 34, 210, 472. See also Auger, *Compt. rend.*, 1921, 172, 1355.

[4] Werther, *J. pr. Chem.*, 1861, 83, 195.

[5] Pissarjewsky, *Zeit. physikal. Chem.*, 1903, 43, 173.

More complex compounds are formed by the action of alkalis and hydrogen peroxide on the pervanadates, and these are probably salts of a pyropervanadic acid with the peroxides of the alkali metals. The ammonium salt, $(NH_4)_4V_2O_{11}$, and the potassium salt, $K_3V_5O_{26},2H_2O$, have been prepared in this way.[1] Complex oxygenated products have also been obtained by the action of hydrogen peroxide on the compound of vanadyl trifluoride with potassium fluoride,[2] $VOF_3,2KF$.

THE LOWER OXIDES OF VANADIUM.

420 *Vanadium Suboxide*, V_2O, is formed by the prolonged exposure of finely divided metallic vanadium to the air. It is a brown substance, which, when heated in the air, is gradually converted into the higher oxides. No salts of this oxide have been prepared.

Vanadium Monoxide or *Hypovanadious Oxide*, VO or V_2O_2.—In its power of uniting with oxygen vanadium surpasses even uranium,[3] and, like uranium, it can be separated from its last portions of oxygen only with extreme difficulty. The oxide VO is, moreover, found to enter as a radicle into many compounds, so that the name vanadyl (VO) may appropriately be given to it. This substance, which was regarded by Berzelius as metallic vanadium, may be prepared by reducing the higher oxides with potassium, or by passing the vapour of vanadyl trichloride, $VOCl_3$, mixed with excess of hydrogen, through a combustion tube containing red-hot carbon.[4] Thus obtained it forms a light-grey, glistening powder or a lustrous, metal-like crust, having a specific gravity of 3·64. It is brittle, difficultly fusible, and conducts electricity. Heated to redness, it takes fire in the air and burns to the sesquioxide, V_2O_3, whilst when heated in chlorine the oxytrichloride, $VOCl_3$, is formed. It is insoluble in water, but dissolves in acids, yielding the corresponding salts. These may also be obtained in solution by the action of nascent hydrogen, evolved by metallic zinc, cadmium, or sodium amalgam, upon a solution made by dissolving vanadium pentoxide in hot concentrated sulphuric acid and then diluting with water, or by the electrolytic reduction of a similar solution. The liquid rapidly changes colour, passing through all shades of blue and green until after some time it assumes a permanent lavender or violet tint. This solution of the sulphate absorbs oxygen with such avidity as to bleach indigo and other vegetable colouring matters as quickly as chlorine. The solution in hydrochloric acid has been suggested as a reagent for removing arsenic from hydrochloric acid, the whole of the arsenic being precipitated in the free state when the impure hydrogen chloride is passed through the solution.[1] On allowing the neutralised lavender-coloured solution to stand exposed to the air for a few seconds, the colour changes to a deep chocolate-brown. The changes in colour which the yellow sulphuric acid solution of vanadium pentoxide undergoes on reduction are exceedingly characteristic, and may be divided into eight stages as follows:

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[1] Melikoff and Pissarjewsky, *Zeit. anorg. Chem.*, 1899, 19, 405; Pissarjewsky, *ibid.*, 1903, 32, 341.

[2] Melikoff and Kasanezky, *Zeit. anorg. Chem.*, 1901, 28, 242.

[3] Péligot, *Ann. Chim. Phys.*, 1842, [3], 5, 5; 1844 [3], 12, 549.

[4] Schafarik, *Annalen*, 1859, 109, 85.

Stage.	Colour.	Reaction.	State of Oxidation of the Metal.
I.	Yellow	Acid	V_2O_5.
II.	Green	Acid	$V_2O_5—VO_2$.
III.	Bluish-green	Acid	$V_2O_5—VO_2$.
IV.	Blue	Acid	VO_2.
V.	Greenish-blue	Acid	$VO_2—V_2O_3$.
VI.	Green	Bleaches slightly	$V_2O_3—VO$.
VII.	Bluish-violet	Bleaches strongly	$V_2O_3—VO$.
VIII.	Lavender or violet	Bleaches strongly	VO.

Thus the salts derived from the pentoxide are yellow; the divanadyl salts blue; the sesqui-salts green; and the vanadious salts lavender-coloured.

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[1] German Patent, 164355 (15/4/04).

Vanadium Sesquioxide or *Vanadium Trioxide*, V_2O_3, is obtained by heating the pentoxide in hydrogen, or by igniting the same oxide in a carbon crucible. It is also formed when vanadyl trichloride and hydrogen are passed through a red-hot tube, and when the pentoxide is heated in the oxy-hydrogen flame.[1] It is a black powder which under pressure forms a coherent mass which conducts electricity. It oxidises when exposed to the air, not only being pyrophoric when warm, but also slowly taking up oxygen when exposed in the air at ordinary temperatures, and being converted into small dark indigo-coloured crystals of the dioxide VO_2. It has a specific gravity of 4·7. When ignited in chlorine gas it is converted into vanadium oxytrichloride, $VOCl_3$, and vanadium pentoxide:

$$3V_2O_3 + 6Cl_2 = V_2O_5 + 4VOCl_3.$$

It is insoluble in most acids, but the corresponding sulphate may be obtained in solution by the reducing action of nascent hydrogen, evolved from metallic magnesium, on a solution of vanadium pentoxide in sulphuric acid. A green liquid is thus obtained, the further reduction observed with zinc, cadmium, and sodium amalgam not taking place with magnesium. The green solution may likewise be obtained by the partial oxidation of the lavender-coloured solution of vanadious sulphate, VSO_4. If a current of air be passed through such a solution, in which the free acid has been neutralised by an excess of zinc and the remaining metallic zinc removed, the liquid attains a permanent brown colour, which with a few drops of acid turns green; the solution then contains the sesquisulphate.

Vanadium Dioxide or *Hypovanadic Oxide*, VO_2 or V_2O_4.—This oxide can be prepared either by the oxidation of the monoxide, VO, in the air, or by the partial reduction of the pentoxide. It is readily converted by potassium permanganate into the pentoxide, and advantage is taken of this fact in the volumetric estimation of vanadium. It is a lustrous, steel-coloured powder and dissolves in acids, forming solutions of the vanadyl salts, which possess a bright blue colour. Solutions of these salts are also produced by the action of moderate reducing agents, such as sulphur dioxide and sulphuretted hydrogen or oxalic acid, upon solutions of vanadic acid in sulphuric acid. They may also be obtained by passing a current of air through acid solutions of the vanadious salts until a permanent blue colour is attained.

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[1] Read, *Journ. Chem. Soc.*, 1894, 65, 314.

The oxide may likewise be prepared by the electrolysis of the fused pentoxide, or by the ignition of the oxychloride, $V_2O_2Cl_4,5H_2O$, in a current of carbon dioxide:

$$V_2O_2Cl_4 + 5H_2O = 2VO_2 + 4HCl + 3H_2O.$$

Divanadyl Hydroxide or *Hypovanadic Hydrate*, $V_2O_4,7H_2O$ or $V_2O_2(OH)_4,5H_2O$, forms a greyish-white precipitate, obtained when a solution of vanadyl sulphate or chloride is cautiously precipitated with a cold solution of sodium carbonate. When dried it is a black, amorphous mass, having a glassy fracture. This on heating to 100° loses four molecules of water, leaving the hydrate, $V_2O_4,3H_2O$. A hydrate containing $2H_2O$ is obtained as a pink, crystalline powder by boiling a solution of the dioxide, VO_2, in sulphurous acid.[1] Vanadium dioxide acts both as a basic, and as an acid-forming oxide. When dissolved in acids the vanadyl salts are formed,[2] whilst with alkalis the vanadites or hypovanadates are produced.

The *vanadites* or *hypovanadates* are all insoluble except those of the alkali metals, which are not derived from the normal hypovanadic acid, $H_4V_2O_6$, but from the partial anhydrides, $H_2V_2O_5$ and $H_2V_4O_9$. The alkali vanadites are obtained by adding an excess of caustic alkali to a concentrated solution of vanadyl sulphate or chloride.[3] The dark-brown solution thus obtained with potash deposits *potassium vanadite*, $K_2V_4O_9,7H_2O$, in reddish-brown, crystalline scales which, after washing first with potash solution, and then with alcohol, may be dried between filter-paper. This salt is permanent in the air, and very soluble in water, yielding a dark brown solution.

Sodium Vanadite, $Na_2V_4O_9,7H_2O$, is prepared in a similar way to the potassium salt, and exhibits analogous properties.

Ammonium Vanadite, $(NH_4)_2V_4O_9,3H_2O$, is obtained as a dark-brown, crystalline precipitate by adding a vanadyl sulphate solution to ammonia; it dissolves in water, yielding an almost black solution (Crow).

VANADIUM AND FLUORINE.

421 The oxides, V_2O_3, VO_2, and V_2O_5, all dissolve in hydrofluoric acid, but only the trifluoride, $VF_3,3H_2O$, and the oxydifluoride, VOF_2, have been isolated. A very large number of

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[1] Gain, *Compt. rend.*, 1906, **143**, 823.

[2] Guyard, *Bull. Soc. chim.*, 1876, [2], **25**, 350.

[3] See also Koppel and Goldmann, *Zeit. anorg. Chem.*, 1903, **36**, 281.

double salts of these compounds and of the oxyfluorides VO_2F and VOF_3 with hydrofluoric acid, metallic fluorides, and vanadium pentoxide have been described.[1] Only a few of the most characteristic are mentioned here.

Vanadium Trifluoride, $VF_3,3H_2O$, crystallises from the dark green solution of vanadium trioxide in hydrofluoric acid, in dark green, readily soluble octahedra. The *double potassium salt*, $2KF,VF_3,H_2O$, is a bright green, crystalline powder, which is precipitated when a solution of potassium fluoride is added to one of vanadium trifluoride.

Vanadium Oxydifluoride, VOF_2, is formed when the tetroxide is dissolved in hydrofluoric acid, and separates in blue, prismatic crystals containing water. Several double salts with the fluorides of sodium, potassium, and ammonium may be prepared by adding solutions of these fluorides to the blue solution of the oxydifluoride (Petersen).

Potassium Vanadium Dioxyfluoride, $2KF,VO_2F$, is obtained by evaporating a solution of vanadium pentoxide in hydrofluoric acid almost to dryness, and adding it to potassium fluoride. It crystallises in golden-yellow, six-sided prisms.

Vanadium pentoxide also dissolves easily in a solution of hydrogen potassium fluoride with evolution of heat, and on cooling yellowish globular masses separate out consisting of pearly, probably hexagonal crystals, which have the composition $3KF,2VO_2F,H_2O$.

Ammonium Vanadium Dioxyfluoride, $3NH_4F,VO_2F$, is formed when a solution of vanadium pentoxide in hydrofluoric acid is nearly neutralised with ammonia; it separates in large, golden-yellow crystals.

Zinc Vanadium Dioxyfluoride, $ZnF_2,VO_2F,7H_2O$, is formed by dissolving zinc carbonate and vanadium pentoxide in hydrofluoric acid. The salt crystallises in hard, yellow, triclinic prisms.

VANADIUM AND CHLORINE.

The following chlorides and oxychlorides of vanadium are known:

CHLORIDES.

Vanadium tetrachloride . .	VCl_4.
" trichloride . . .	VCl_3 or V_2Cl_6.
" dichloride . .	VCl_2 or V_2Cl_4.

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[1] Petersen, *J. pr. Chem.*, 1889, [2], 40, 193, 271. See also Piccini and Giorgis, *Journ. Chem. Soc.*, 1889, 56, 214; and Baker, *Journ. Chem. Soc.*, 1878, 33, 388.

OXYCHLORIDES.

Vanadium oxytrichloride	$VOCl_3$.
„ oxydichloride	$VOCl_2$.
„ oxymonochloride	$VOCl$.
Divanadyl monochloride	V_2O_2Cl.
„ tetrachloride	$V_2O_2Cl_4,5H_2O$.
Divanadium trioxydichloride	$V_2O_3Cl_2,4H_2O$.

Vanadium Tetrachloride, VCl_4, is formed when metallic vanadium or the mononitride is heated to redness in an excess of chlorine. It may be prepared by repeatedly passing the vapour of vanadium oxytrichloride, together with an excess of dry chlorine, over a long column of pure sugar-charcoal heated to dull redness; also, by treating the crude vanadium, prepared as already described by the aid of aluminium, with chlorine and removing the oxytrichloride, which is also formed, by fractional distillation;[1] or by heating ferrovanadium in chlorine.[2] Vanadium tetrachloride is a dark brownish-red, thickish liquid, which evolves white fumes when exposed to moist air. It boils at 154° with partial decomposition, losing chlorine and leaving a residue of the trichloride. This decomposition takes place also at the ordinary temperature, especially on exposure to light. It does not solidify at $-18°$; its specific gravity at 0° is 1·8584, and its vapour density at 205° is 6·69, the calculated vapour density being 6·675. When thrown into water the tetrachloride is at once decomposed, yielding a blue solution of vanadyl chloride. It is soluble in carbon tetrachloride.

Vanadium Trichloride, VCl_3.—The foregoing compound easily decomposes, as has been stated, into this body and chlorine. The trichloride is obtained either by the slow decomposition of the tetrachloride at the ordinary temperature or at its boiling point, or, together with the dichloride, when the vapour of the tetrachloride mixed with hydrogen is passed through a red hot tube, as well as when the trisulphide is heated in chlorine.[3] It crystallises in fine peach-blossom coloured, shining tablets of density 3·0, closely resembling in appearance the crystals of chromium trichloride. It is non-volatile when heated in hydrogen, which reduces it to the dichloride, and decomposes to the pentoxide when heated in the air. It is extremely hygroscopic, instantly deliquescing on exposure to moist air to a dark brown liquid, which on addition of a drop of hydrochloric acid becomes green. It readily dissolves in absolute alcohol and in ether, forming green-coloured solutions.

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[1] Koppel, Goldmann and Kaufmann, *Zeit. anorg. Chem.*, 1905, **45**, 345.

[2] Mertes, *J. Amer. Chem. Soc.*, 1913, **35**, 671.

[3] Halberstadt, *Ber.*, 1882, **15**, 1619.

A hydrated compound of the composition $VCl_3,6H_2O$ can be obtained as a green, crystalline powder by evaporating *in vacuo* a solution of vanadium sesquioxide in hydrochloric acid,[1] or by dissolving vanadium pentoxide in hydrochloric acid, reducing the solution electrolytically with a platinum cathode, and saturating the green solution with hydrochloric acid.[2] The salt decomposes when heated before all the water has been driven off. The aqueous solution rapidly oxidises in the air. Sparingly soluble double salts are formed with the chlorides of the alkali metals,[3] the potassium salt having the formula $VCl_3,2KCl,H_2O$.

Vanadium Dichloride or *Vanadious Chloride*, VCl_2.—This is a solid body, crystallising in fine apple-green coloured plates, having a micaceous lustre and a hexagonal form. It is prepared by passing vanadium tetrachloride, mixed with dry and pure hydrogen, through a glass tube heated to dull redness, and is also formed together with silicon tetrachloride when vanadium silicide, VSi_2, is heated in chlorine.[4] Its specific gravity at 18° is 3·23. It is very deliquescent, yielding a lavender-coloured solution of vanadium dichloride, which possesses bleaching properties (p. 958). A violet solution containing the chloride can be obtained by the electrolytic reduction of the trichloride. When it is evaporated or when hydrochloric acid is added, hydrogen is evolved and the trichloride is formed, the reaction being extremely vigorous when a piece of platinum foil is placed in the acid liquid. Vanadious chloride is therefore a more vigorous reducing agent than chromous chloride.[5]

Vanadium Oxytrichloride or *Vanadyl Trichloride*, $VOCl_3$.—This compound, corresponding to phosphorus oxychloride, is obtained either by the action of chlorine on the oxides VO and V_2O_3 as already described, or by heating a mixture of the pentoxide and charcoal in a current of chlorine:

$$V_2O_5 + 3C + 3Cl_2 = 2VOCl_3 + 3CO.$$

In the latter case, the resulting liquid is red-coloured from the presence of tetrachloride, and is best purified by rectification

[1] Locke and Edwards, *Amer. Chem. J.*, 1898, **20**, 594.

[2] Piccini and Brizzi, *Zeit. anorg. Chem.*, 1899, **19**, 394.

[3] Stähler, *Ber.*, 1904, **37**, 4411.

[4] Moissan and Holt, *Compt. rend.*, 1902, **135**, 78.

[5] Piccini and Marino, *Zeit. anorg. Chem.*, 1902, **32**, 68.

over clean sodium in a current of carbon dioxide. It is also formed[1] when dry hydrogen chloride is passed over a mixture of vanadic and phosphoric anhydrides at 60—80°, and a solution in acetic acid may be obtained by treating vanadium pentoxide with a solution of hydrogen chloride in glacial acetic acid.[2] Vanadyl trichloride is a bright lemon-yellow, mobile liquid, boiling at 126·7° and having a specific gravity at 14° of 1·841. It does not solidify at −15°. The specific gravity of its vapour is 6·108 at 186°, the calculated specific gravity being 6·003.

On exposure to moist air vanadyl trichloride emits vapours of a cinnabar-red colour, and is soon decomposed in the presence of moisture into vanadic and hydrochloric acids. When a small quantity of water is added it becomes thick and blood-red coloured owing to the formation of vanadic acid. A large quantity of water, however, yields a clear yellow solution.[3] When the oxychloride is ignited in a current of dry ammonia gas, vanadium mononitride is obtained. Vanadium oxychloride combines with ether at 70°, forming a compound crystallising in long, red needles and having the composition $VCl_3(OC_2H_5)_2$.[4]

When vanadium oxychloride is heated with zinc to 400°, vanadium dioxide and *vanadyl dichloride*, $VOCl_2$, are formed; the latter crystallises in green tablets which deliquesce on exposure to moist air. The same compound is formed when the vapour of vanadyl trichloride and hydrogen are passed through a red hot tube. In this case *vanadyl monochloride*, $VOCl$, and *divanadyl monochloride*, V_2O_2Cl, are likewise formed, the former as a flocculent, brown powder insoluble in water, and the latter in the form of a yellow, crystalline powder resembling mosaic gold. The molecular formulæ of these bodies are not known. Vanadyl dichloride forms double compounds with two or four molecules of the hydrochlorides of pyridine and quinoline.[5]

Divanadyl Tetrachloride, $V_2O_2Cl_4,5H_2O$ or $VOCl_2,2·5H_2O$. When vanadium pentoxide is dissolved in hot concentrated hydrochloric acid, chlorine is evolved and a green solution is obtained which becomes blue with deposition of sulphur when sulphuretted hydrogen is passed through the liquid. A brown, amorphous, deliquescent mass is obtained on evaporation, possessing the above composition. It dissolves in water, yielding a blue solution; but when treated with strong hydrochloric acid or alcohol the solution is brown, and this change may possibly be due to the existence of two different hydrates.[1]

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[1] Ephraim, *Zeit. anorg. Chem.*, 1902, **35**, 60.

[2] Koppel and Kaufmann, *Zeit. anorg. Chem.*, 1905, **45**, 352.

[3] See Agafonoff, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 649.

[4] Bedson, *Journ. Chem. Soc.*, 1876, i, 309.

[5] Koppel, Goldmann and Kaufmann, *Zeit. anorg. Chem.*, 1905, **45**, 345.

A compound of the formula $V_2O_3Cl_2,4H_2O$ has also been obtained as a dark green, deliquescent mass, by the action of hydrochloric acid on vanadium pentoxide.[2]

VANADIUM AND BROMINE AND IODINE.

423 *Vanadium Tribromide*, VBr_3.—This is the only known compound of the above elements. It condenses as a greyish-black, compact, amorphous sublimate when dry bromine vapour is passed in excess over vanadium nitride or over a mixture of vanadium trioxide and charcoal heated to redness. It is a very unstable compound. losing bromine even at the ordinary temperature in dry air, and deliquescing rapidly in moist air.

The hydrated bromide, $VBr_3,6H_2O$, and the corresponding iodide can be prepared in a similar manner to the hydrated chloride, which they closely resemble.

Vanadyl Tribromide, $VOBr_3$, obtained by passing dry bromine vapour over vanadium sesquioxide heated to redness, is a dark red, transparent liquid, having a density of 2·967 at 0°. It may be distilled under diminished pressure, passing over without decomposition at a temperature of about 130° under a pressure of 100 mm. When heated under the ordinary atmospheric pressure it suddenly solidifies at 180°, decomposing into free bromine and *vanadyl dibromide*, $VOBr_2$, which is a brownish-yellow powder.

Divanadyl Tetra-iodide, $V_2O_2I_4,8H_2O$, is formed by the action of hydriodic acid on the pentoxide as a dark, deliquescent mass.[3]

VANADIUM AND SULPHUR.

424 The sulphides of vanadium correspond to the oxides.[4]

Vanadium Monosulphide, VS, is formed when the sesquisulphide is strongly heated in a current of hydrogen. It forms a brownish-black powder or glistening brown scales, soluble slowly in dilute, quickly in strong nitric acid. It dissolves in alkali hydrosulphides, yielding a violet solution.

Vanadium Sesquisulphide or *Trisulphide*, V_2S_3.—This was the only vanadium salt free from oxygen prepared by Berzelius. He obtained it by heating the sesquioxide in a current of sulphuretted hydrogen. It can in like manner be prepared from the pentoxide, the oxychloride, or any of the chlorides, but it is best obtained by acting on the ignited pentoxide with carbon disulphide vapour. It is a greenish-black powder possessing properties similar to those of the monosulphide, VS.

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[1] Crow, *Journ. Chem. Soc.*, 1876, ii., 453.

[2] Ditte, *Compt rend.*, 1886, 102, 1310.

[3] *Ibid.*

[4] Kay, *Journ. Chem. Soc.*, 1880, 37, 728.

Vanadium Pentasulphide, V_2S_5, is formed by heating the foregoing with sulphur to 400°. It is a black powder which on heating in a current of carbon dioxide yields sulphur and the sesquioxide (Kay).

Ammonium Thiovanadate, $(NH_4)_3VS_4$, is obtained by passing sulphuretted hydrogen into a cooled solution of ammonium metavanadate in ammonia of specific gravity 0·898. The crystals resemble those of potassium permanganate. If weaker ammonia be employed, *ammonium hexasulphopyrovanadate*, $(NH_4)_4V_2S_6O$, is formed in dark green crystals.

Several similar sodium and potassium salts have been prepared from the corresponding meta- and pyro-vanadates.[1]

Vanadyl or *Hypovanadic Sulphite*, $6VO_2,4SO_2,9HO$, is prepared by reducing barium vanadate with sulphur dioxide, and filtering from the barium sulphate:

$$Ba(VO_3)_2 + H_2SO_3 = BaSO_4 + H_2O + 2VO_2.$$

When the filtrate is evaporated in an atmosphere of sulphur dioxide, the sulphite separates as a dark blue, crystalline powder, which spontaneously decomposes. It forms two series of double salts with the alkali sulphites.[2]

Vanadious Sulphate, $VSO_4,7H_2O$, can be prepared by the electrolytic reduction of the blue solution obtained by the action of sulphur dioxide on vanadic anhydride in the presence of sulphuric acid. In order to obtain this salt in the pure state the greatest precautions must be taken to exclude oxygen. The blue solution gradually becomes green, then blue again, and finally violet as the reduction proceeds. It is then evaporated *in vacuo*, and the crystals are separated and dried with filter paper in an atmosphere of carbon dioxide. The salt is thus obtained in reddish-violet, monoclinic crystals, which become bluish-violet on drying and are very soluble in water, yielding a pure violet-coloured solution, which becomes bluish-violet in the presence of the slightest trace of oxygen. The solution at once reduces copper salts to metallic copper, the reaction proceeding quantitatively thus:

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[1] Krüss and Ohnmais, *Annalen*, 1891, **263**, 39; Krüss, *Zeit. anorg. Chem.*, 1893, **3**, 264; Locke, *Amer. Chem. J.*, 1898, **20**, 373.

[2] Koppel and Berendt, *Zeit. anorg. Chem.*, 1903, **35**, 154; Gain, *Compt. rend.*, 1907, **144**, 1157.

$$2VSO_4 + CuSO_4 = V_2(SO_4)_3 + Cu.$$

The salts of silver, tin, gold, platinum, and mercury are also reduced to the metal.

Vanadious sulphate appears to be isomorphous with ferrous sulphate, $FeSO_4,7H_2O$, and mixed crystals have been obtained both with ferrous sulphate and with magnesium sulphate. It readily forms double salts of the type $R^I_2SO_4,R^{II}SO_4,6H_2O$ with the alkali sulphates. These can be prepared by adding the proper sulphate to the liquid to be reduced and crystallising, etc., as in the preparation of the pure sulphate. The *ammonium* salt, $(NH_4)_2SO_4,VSO_4,6H_2O$, forms reddish-violet, monoclinic crystals and is less easily oxidised than the pure sulphate, and the potassium and rubidium salts closely resemble it.[1]

Vanadium Sesquisulphate, $V_2(SO_4)_3$.—When the blue solution of vanadyl sulphate, prepared from 100 grams of vanadic anhydride, 200 c.c. of water, and 100 c.c. of concentrated sulphuric acid, is reduced electrolytically until the vanadium is present in the trivalent form, the compound $V_2(SO_4)_3,H_2SO_4,12H_2O$, known as *vanadium sesquisulphate sulphuric acid*, separates out as a green, crystalline powder. It readily forms a salt when evaporated with ammonium sulphate, green crystals separating out of the composition $V_2(SO_4)_3,(NH_4)_2SO_4,12H_2O$.

When the acid salt is dissolved in a little water, sulphuric acid added, and the mass heated at 180° in a current of carbon dioxide, the anhydrous sulphate separates out as a microcrystalline, yellow powder which is insoluble in water.[2] These compounds have a very close resemblance to the corresponding derivatives of titanium sesquioxide (p. 835). A solution of the sulphate acts as a vigorous reducing agent, and precipitates the metal from an acid solution of copper sulphate (Rutter).

Vanadium Alums.—Several alums have been prepared by treating a metavanadate with sulphurous acid in the presence of sulphuric acid, and then reducing electrolytically. *Ammonium*

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[1] Piccini, *Zeit. anorg. Chem.*, 1899, 19, 204; Piccini and Marino, *Zeit. anorg. Chem.* 1902, 32, 55; Marino, *Zeit. anorg. Chem.*, 1906, 50, 49; Rutter, *Zeit. Elektrochem.*, 1906, 12, 230; *Zeit. anorg. Chem.*, 1907, 52, 368.

[2] Stähler and Weithwein, *Ber.*, 1905, 38, 3978.

vanadium alum, $(NH_4)_2SO_4,V_2(SO_4)_3,24H_2O$, crystallises in hemihedral forms of the regular system and is violet-coloured. Alums containing potassium, rubidium, cæsium, and thallium have also been prepared.[1] A good yield of the alum is obtained by the electrolysis of ammonium metavanadate. The ammonium metavanadate is placed in a porous cell with 50 per cent. sulphuric acid, a lead cathode being employed. The electrolysis is continued until the solution becomes green, when on standing ammonium vanadium alum crystallises out.[2]

The Vanadyl or Hypovanadic Sulphates.—The blue solution obtained by the action of sulphur dioxide on a suspension of vanadic anhydride in dilute sulphuric acid contains sulphates of the radical $V_2O_2^{IV}$ or VO''. These were termed hypovanadic sulphates by Roscoe, but are now generally known as the vanadyl sulphates. From all solutions in which the molecular ratio $H_2SO_4 : VO_2$ is greater than 1·5 : 1, acid sulphates are obtained up to a temperature of about 201·5°; from solutions in which the ratio is less than this normal salts are obtained, and these are also formed by heating the acid sulphates to about 260°, or by treating them with water or alcohol. At the boiling point of sulphuric acid oxidation occurs, vanadic anhydride and sulphur dioxide being formed (Koppel and Behrendt).

Vanadyl Sulphate, $V_2O_2(SO_4)_2$, is deposited as an insoluble, blue, sandy powder by dissolving the dioxide, VO_2, in excess of sulphuric acid and heating the solution for some time to 260°.[3] If the dioxide be dissolved in sulphuric acid, the solution evaporated, and the residue treated with absolute alcohol, a sky-blue powder remains, which is a soluble form of the sulphate and deliquesces in moist air. This is also formed by heating the insoluble form with water at 130°. If the solution be allowed to evaporate spontaneously over sulphuric acid, fine, blue, rhombic prisms having the composition $V_2O_2(SO_4)_2,4H_2O$ are deposited (Berzelius). In addition to this, hydrates with 13, 10, 7, 3, and 2 molecules of water have been described.

When the acid solution containing more than 1·5 molecular proportions of sulphuric acid is evaporated, various hydrates of the *acid salt*, $(V_2O_2)H_2(SO_4)_3$ are obtained. The hydrate with

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[1] Piccini, *Zeit. anorg. Chem.*, 1896, 11, 106; *Chem. Centr.*, 1897, i, 223; Bültemann, *Zeit. Elektrochem.*, 1904, 9, 141.

[2] Renschler, *Zeit. Elecktrochem.*, 1912, 18, 137.

[3] Gerland, *Ber.*, 1877, 10, 2109; Koppel and Behrendt, *Zeit. anorg. Chem.*, 1903, 35, 154.

$5H_2O$ is prepared by evaporating the solution on the water-bath, and washing the dried crystals with ether (Crow); at 125° the hydrate with $3H_2O$ is formed, and this can also be obtained by precipitating a concentrated solution of any of the vanadyl sulphates with concentrated sulphuric acid. At 150° the dihydrate is formed, at 175° a salt with 0·5 molecule of water, and at 190° the *anhydrous compound*, $2VO_2,3SO_3$, which is a green powder, consisting of microscopic tetragonal tablets, and is sparingly soluble in water (Koppel and Behrendt).[1]

Many double salts also of this series are known and are described in the memoirs cited above.

Normal Divanadyl Trisulphate, $(VO)_2(SO_4)_3$, is obtained, according to Berzelius, by dissolving the pentoxide in hot sulphuric acid which has been diluted with half its weight of water.[2] On evaporating at a low temperature the salt crystallises out in reddish-brown, very deliquescent scales. The same compound is obtained in ruby-red octahedra by boiling the pentoxide with an excess of sulphuric acid. When these are heated to the melting point of lead, the basic salt, $(VO)_2O(SO_4)_2$, remains as a red mass with small, bright, crystalline faces.

If the pentoxide be dissolved in concentrated sulphuric acid and the solution evaporated, the basic salt, $VO(OH)SO_4$, is formed[3] as a sandy, reddish-yellow powder. According to Gerland, this is identical with the preceding compound.

When potassium vanadate is dissolved in strong sulphuric acid and the excess of acid driven off by heat, the double salt, $K_2SO_4,(VO)_2(SO_4)_3$, is obtained as a yellow, crystalline powder, (Berzelius).

VANADIUM AND NITROGEN, PHOSPHORUS, AND ARSENIC.

425 *Vanadium Mononitride*, VN.—The mononitride is obtained by strongly igniting the ammonio-oxychloride in a current of dry ammonia (or rather of its component gases) at a white heat as a greyish-brown powder, which does not undergo change at ordinary temperatures. It is likewise obtained when the black residue left on calcining ammonium metavanadate in the air is heated to whiteness in a current of dry ammonia. Other methods of obtaining the nitride are to expose the oxide or dichloride to the action of ammonia gas at a white heat.

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[1] See also Gain, *Compt. rend.*, 1906, 143, 1154.

[2] See also Ditte, *Compt. rend.*, 1886, 102, 757.

[3] Gerland, *Ber.*, 1878, 11, 98.

When heated in the air, vanadium mononitride glows and slowly oxidises to the blue oxide; when heated with soda-lime, ammonia is produced.

Vanadium Dinitride, VN_2, is obtained as a black powder by passing ammonia over vanadyl trichloride, heating the residue in a glass tube to expel ammonium chloride, washing with water, and drying in a vacuum over sulphuric acid.

426 Extended series of phosphovanadic and arsenovanadic acids and their derivatives have been described by Berzelius,[1] Ditte,[2] and Gibbs.[3] According to Friedheim[4] these substances are phosphates and arsenates of vanadium (and double salts of these with the vanadates), in which vanadic anhydride acts as a weak base, the radical VO_2 replacing one or two hydrogen atoms of phosphoric or arsenic acid. They can be prepared by bringing the requisite salts together.

Phosphovanadic Acid, $2(VO_2)H_2PO_4,9H_2O = P_2O_5,V_2O_5,11H_2O$, is formed when vanadic anhydride is heated with syrupy phosphoric acid, and crystallises in golden-yellow flakes.

Arsenovanadic Acid, $As_2O_5,V_2O_5,10H_2O$, is prepared in a similar manner, and forms yellow crystals.

VANADIUM AND THE ELEMENTS OF THE CARBON GROUP.

427 *Vanadium Carbide*, VC, is formed when vanadic anhydride is heated with carbon in the electric furnace. It forms hard crystals of the specific gravity 5·405, burns in oxygen, and becomes incandescent when heated in chlorine.[5] It is silvery-white, very hard, and melts at 2750°.[6]

Vanadium Cyanides.—Double salts of vanadium dicyanide and tricyanide with potassium cyanide of the formulæ $K_4V(CN)_6,3H_2O$ and $K_3V(CN)_6$ have been prepared.[7]

Potassium Vanadic Thiocyanate, $V(SCN)_3,3KSCN,4H_2O$, is prepared in a similar manner to the cyanide (Locke and Edwards), and separates in dark red crystals, the solution of which in water rapidly decomposes. The ammonium and sodium salts have also been obtained.[8]

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[1] *Lehrbuch*, [6], **3**, 1037.

[2] *Compt. rend.*, 1886, **102**, 757.

[3] *Amer. Chem. J.* 1885–6, **7**, 118, 209.

[4] *Ber.*, 1890, **23**, 1530, 2600.

[5] Moissan, *Compt. rend.*, 1896, **122**, 1297.

[6] Ruff and Martin, *Zeit. angew. Chem.*, 1912, **25**, 49.

[7] Petersen, *Zeit. anorg. Chem.*, 1904, **38**, 342; Locke and Edwards, *Amer. Chem. J.*, 1898, **20**, 594.

[8] Cioci, *Zeit. anorg. Chem.*, 1899, **19**, 308.

Complex ammonia vanadyl thiocyanates and oxalates have likewise been prepared.[1]

Vanadium and Silicon.—Vanadium forms two compounds with silicon. The *silicide*, V_2Si, is prepared[2] by heating 120 parts of the sesquioxide with 14 of silicon in the electric furnace, or better by heating this mixture with either carbon or copper. It forms hard, silver-white prisms with a metallic lustre, and has the sp. gr. 5·48 at 17°. It is only attacked by fluorine when gently heated, and it is readily decomposed when heated in chlorine, bromine, or hydrogen chloride. It is insoluble in acids, with the exception of hydrofluoric acid, and is decomposed by fused potash. When it is fused with silicon it is converted into the *disilicide*, VSi_2, which can be obtained also by heating the sesquioxide with an excess of silicon in the electric furnace, or by igniting a mixture of the oxide and silicon with metallic magnesium.[3] It forms hard prisms with a metallic lustre, has the sp. gr. 4·42, and melts and volatilises in the electric furnace. It is soluble in hydrofluoric acid, burns when heated in fluorine, chlorine, or bromine, and is attacked by gaseous hydrogen chloride. It is also decomposed by fused alkalis, and by molten copper, an alloy of this metal with vanadium being formed.

DETECTION AND ESTIMATION OF VANADIUM.

428 Insoluble vanadium compounds can be brought into solution by treatment either with acids or with alkalis. The hydrochloric acid solution assumes a bright blue colour on the addition of zinc. A solution of vanadyl sulphate cannot be distinguished in colour from one of copper sulphate when diluted to the requisite extent with water. It, however, of course, does not become colourless in presence of metallic iron. Solutions of certain vanadates also closely resemble solutions of the chromates. Thus, for instance, a solution of the tetravanadate of potassium does not differ in appearance from one of potassium dichromate. They may, however, be distinguished from one another, inasmuch as the vanadate solution becomes blue, whilst the chromate assumes a green colour, on reduction. When a solution of vanadic acid or an acid solution of an alkali vanadate is shaken up with ether containing hydrogen peroxide, the aqueous solution assumes a red colour like that of ferric

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[1] Koppel and Goldmann, *Zeit. anorg. Chem.*, 1903, **36**, 281.

[2] Moissan and Holt, *Compt. rend.*, 1902, **135**, 493.

[3] *Ibid.*, 78.

acetate. This reaction serves to detect 1 part of vanadic acid in 40,000 parts of the liquid, and is not affected by the presence of chromic acid.[1]

For the *quantitative* estimation of vanadium in a soluble vanadate it may be treated with lead acetate, when basic lead vanadate is precipitated. The precipitate is insoluble in acetic acid but it dissolves readily in nitric acid, liberating vanadic acid, which separates out, but dissolves completely when the liquid is warmed. In the analysis of a soluble vanadate this insoluble lead salt is collected on a filter, dried at 100°, and weighed; a given quantity of the dried salt is then dissolved in nitric acid, the lead precipitated by pure sulphuric acid, and the lead sulphate estimated with the usual precautions by evaporation, addition of alcohol, etc., or the filtrate is evaporated and the residue heated and weighed as vanadic anhydride.[2] The lead sulphate thus obtained is quite free from vanadium, whilst the vanadium pentoxide in the filtrate is obtained perfectly pure and well crystallised on evaporation and ignition. The filtrate from the lead vanadate, freed from excess of lead by means of sulphuric acid and evaporated, yields the alkali sulphate, containing no trace of vanadium. Vanadium may be very readily estimated volumetrically when no other reducible metals are present. For this purpose the solution of vanadic acid in sulphuric acid is diluted and reduced to a vanadyl salt by passing a current of sulphur dioxide through it and afterwards boiling to expel the excess of this gas. Standard permanganate is then added until a permanent coloration is obtained. The inverse process may also be employed, and the acid solution of a vanadate titrated with decinormal ferrous sulphate solution, potassium ferricyanide being employed as indicator.[3] Under these circumstances the acid is reduced to VO_2 and the process can be carried out in the presence of copper. The reduction may also be effected by repeated evaporation with hydrochloric acid.[4]

The Atomic Weight of vanadium has been determined in several ways. One is by igniting vanadium pentoxide in dry hydrogen, when it is reduced to the sesquioxide, and the atomic weight of vanadium is deduced from the loss in weight.

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[1] G. Werther, *J. pr. Chem.*, 1863, **88**, 195.

[2] Corminbœuf, *Ann. Chim. anal.*, 1902, 7, 258.

[3] Williams, *J. Soc. Chem. Ind.*, 1902, **21**, 389.

[4] Campagne, *Ber.*, 1903, **36**, 3164. See also Gooch and Stookey, *Amer. J. Sci.*, 1902, [4], **14**, 369; Gooch and Gilbert, *Zeit. anorg. Chem.*, 1903, **35**, 420; Nakazono, *J. Chem. Soc. Japan*, 1921, **42**, 761.

In this manner Roscoe[1] obtained the value 51·38. A second and more trustworthy method for the determination of the atomic weight of vanadium is the analysis of vanadyl trichloride. The chlorine in this compound was estimated by Roscoe both volumetrically and gravimetrically, the results being 51·06 and 51·26 respectively. The gravimetric analysis of vanadyl trichloride by Prandtl and Bleyer[2] yielded the value 51·07, while McAdam,[3] by the conversion of sodium vanadate into sodium chloride found 50·97. A still further determination by Briscoe and Little,[4] who analysed vanadyl trichloride, gave the value 50·96, in close agreement with that of McAdam. The value now adopted (1922) for the atomic weight of vanadium is 51·0.

COLUMBIUM. Cb = 93·1. At. No. 41.

429 This metal is so closely connected with the next member of the same group, tantalum, that it will be most convenient to consider their history together.

In the year 1801, Hatchett[5] laid before the Royal Society an investigation on a mineral known as columbite, from Massachusetts, which he believed to contain a new metal to which he gave the name *columbium*. In the following year, Ekeberg,[6] in Sweden, investigating the yttrium minerals, discovered a new element in a mineral to which he afterwards gave the name of yttrotantalite, whilst the same element also occurred in a mineral termed tantalite. In consequence of this he named the metal *tantalum*, partly because mythological names were frequently used, and partly also as pointing to the fact "that when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them."

In 1809, Wollaston[7] endeavoured to show that columbium and tantalum were identical, and a few years later Berzelius[8] more carefully investigated the oxides of the last-named metal obtained from tantalite, and prepared tantalic acid. Afterwards, in 1839, Wöhler[1] found that the acid-forming oxide contained in pyrochlor and in the Bavarian tantalites possessed peculiar properties; and Rose[2] then observed that the columbites of Bodenmais contained the oxide of a new metal, to which he gave the name of niobium (Nb), and in 1846 he thought that he had found a third new metal, to which he gave the name of *pelopium*. In 1853 he came to the conclusion on further investigation that niobic acid and pelopic acid were different oxides of niobium, and to the first of these he gave the name of niobic acid, whilst the latter was designated as hyponiobic acid. These, however, exhibited "a relationship so peculiar that the whole range of chemistry does not furnish an example of a similar kind."[3] In 1856–7 Hermann observed that niobium and tantalum usually occurred together, whilst in 1864–5, Blomstrand[4] showed that Rose's hyponiobic chloride contained oxygen, and was an oxychloride, and Marignac[5] almost at the same time proved that the double salts which hyponiobic fluoride forms with metallic fluorides are isomorphous with similar double salts containing titanium fluoride, TiF_4, and tungsten oxyfluoride, WO_2F_2. Inasmuch as the sum of the atoms in all these isomorphous compounds is constant, and as, according to analysis, the hyponiobic fluoride contains three atoms of fluorine for one of oxygen, Marignac concluded that it must be an oxyfluoride of the composition $NbOF_3$, and he succeeded in obtaining experimental evidence of the truth of this view. At the same time, he showed that tantalic acid, which up to that time had been supposed to be analogous to titanic acid, and to which the formula TaO_2 had been given, must, like the highest oxide of niobium, be a pentoxide, as these two oxides occur in isomorphous mixture in several minerals, and as both metals form isomorphous double fluorides, such as K_2TaF_7 and K_2NbF_7.

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[1] *Phil. Trans.*, 1868, **158**, 6.

[2] *Zeit. anorg. Chem.*, 1909, **65**, 152; 1910, **67**, 257.

[3] *J. Amer. Chem. Soc.*, 1910, **32**, 1603.

[4] *Journ. Chem. Soc.*, 1914, **105**, 1310.

[5] *Phil. Trans.*, 1802, **92**, 49.

[6] *Ann. Chim.*, 1802, **43**, 276.

[7] *Phil. Trans.*, 1809, **99**, 246.

[8] *Pogg. Ann.*, 1820, **4**, 6.

The name columbium, originally proposed by Hatchett, has always been employed in America for Rose's niobium, and has recently also been adopted in England, whilst in Germany the name niobium is retained.

The truth of this view of the composition of the columbium and tantalum compounds was confirmed by the experiments of Deville and Troost,[6] who in 1865 determined the vapour densities of columbium chloride, columbium oxychloride, and tantalum chloride, which were found to correspond to the formulæ $CbCl_5$, $CbOCl_3$, and $TaCl_5$. The investigations of Blomstrand and Marignac next showed that the metal *dianium*, supposed by v. Kobell to be contained in various columbites, is in fact identical with columbium, and Marignac further showed that *ilmenium*, which Hermann believed he had discovered in samarskite, is a mixture of columbium and tantalum. It appears certain that *neptunium*, also discovered by Hermann, is a similar mixture.[1]

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[1] *Pogg. Ann.*, 1839, **48**, 91.

[2] *Ibid.*, 1844, **63**, 307, 693; 1846, **69**, 116.

[3] *Ibid.*, 1853, **90**, 471.

[4] *J. pr. Chem.*, 1866, **97**, 37.

[5] *Ann. Chim. Phys.*, 1866, [4], **8**, 5, 49.

[6] *Compt. rend.*, 1865, **60**, 1221.

430 The only tantalum ore of commercial importance is *tantalite*, FeO,Ta_2O_5, or ferrous tantalate, which is a black mineral the density of which varies from 6·5 to 7·3. Part of the tantalum is invariably replaced by columbium, and part of the iron by manganese, until in *manganotantalite*, MnO,Ta_2O_5, manganese is the chief metal present. *Microlite*, or calcium tantalate, CaO,Ta_2O_5, is also known, while a very interesting mineral is *stibiotantalite*, $(SbO)_2Ta(Cb)_2O_6$.

Columbite, FeO,Cb_2O_5, is the most commonly occurring columbium-tantalum mineral. Part of the columbium is always replaced by tantalum, and manganese accompanies the iron. The density varies from 5·3 to 6·5, increasing with increase in the content of tantalum. Like tantalite, the mineral crystallises in orthorhombic prisms.

Columbite and tantalite have been found in Scandinavia, Finland, Russia, Greenland, Bavaria, Ceylon, Malay States, in Dakota and other parts of the United States, and particularly in Western Australia, in the Pilbara and Greenbushes gold-mining districts.[2] The Pilbara district is the most important, and produces almost entirely manganotantalite. The accompanying table records the analyses of various samples of the minerals already mentioned. (See Table on p. 976.)

Of the numerous other columbium–tantalum minerals, several may be briefly mentioned, since they also contain the rare earths. *Æschynite*, $Ce_2Cb_4O_{13},Ce_2(TiTh)_5O_{13}$, is essentially a columbo-titanate of the cerite earths, containing thorium in considerable quantity. It is found in Norway and the Urals. *Fergusonite*, $(Y,Ce)(Cb,Ta)O_4$, is a metacolumbate of the yttrium earths

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[1] See Smith, *Proc. Amer. Phil. Soc.*, 1905, **44**, 151; Hall and Smith, *J. Amer. Chem. Soc.*, 1905, **27**, 1309; Barr, *ibid.*, 1908, **30**, 1668; Hildebrand, *ibid.*, 1908, **30**, 1672.

[2] See Simpson, *Chem. News*, 1909, **99**, 49, 77.

Mineral.	Tantalite.		Columbite.		Mangano-tantalite.	Microlite.	Stibio-tantalite.
Locality.	Greenbushes.	Sweden.	Greenland.	Massachusetts.	Pilbara.	Pilbara.	Greenbushes.
Ta_2O_5	80·61	49·64	77·97	28·55	68·65	77·16	51·95
Cb_2O_5	2·50	29·27		51·53	15·11		4·49
WO_3	0·13	—	0·13	0·76	—	—	—
SnO_2	1·51	2·49	0·73	0·34	0·48	—	—
TiO_2	0·71	—	—	—	0·40	—	—
ZrO_2	—	—	0·13	0·24	—	—	—
SiO_2	—	—	—	—	—	—	3·14
FeO	10·89	13·77	17·33	13·54	1·63	3·64	—
Fe_2O_3	—	—	—	—	—	—	0·39
MnO	3·78	2·88	3·28	4·55	14·15	0·60	—
CaO	—	—	—	—	—	13·46	—
MgO	0·19	—	0·23	0·42	0·15	0·42	—
PbO	—	—	0·12	—	—	—	—
$Na(K)_2O$	—	—	—	—	—	1·86	—
Sb_2O_3	—	—	—	—	—	—	38·04
Bi_2O_3	—	—	—	—	—	—	0·79
CuO	—	—	—	—	—	—	0·20
H_2O	0·14	—	—	0·16	0·07	1·28	0·61
Analyst.	Simpson.	Rammelsberg.	Blomstrand.		Simpson.		

containing also thorium and uranium. It occurs in Greenland, Scandinavia, and various localities in the United States. *Yttrotantalite* and *samarskite* are columbo-tantalates of yttrium, iron, and calcium, the latter mineral containing considerable amounts of uranium. Samarskite occurs massive in North Carolina, and has also been found in India. *Euxenite* is an orthorhombic columbo-titanate of yttrium, containing uranium; the isomorphous mineral *polycrase* is similar in composition, but contains less columbium and more titanium.

Besides occurring in these and other minerals, columbium and tantalum are frequently found in small quantities in tinstone, wolfram, pitchblende, monazite, and other minerals.

For the purpose of preparing columbium and tantalum compounds, it is best to start with columbite or tantalite, which contain very little titanium, rather than to employ one or other of the minerals rich in titanium, since no methods are yet known for the quantitative separation of columbium and tantalum from titanium, at any rate when operating on a fairly large scale. For decomposing the mineral, Giles[1] strongly recommends fusion of the finely powdered substance with 2½ to 3 times its weight of potassium carbonate in a steel or wrought-iron crucible. The fusion is carried out in a reducing atmosphere by placing the crucible, covered with a lid, inside a larger crucible, the inner crucible being completely surrounded with charcoal. In this manner the columbium and tantalum are transformed into potassium columbate and tantalate, which may be extracted from the fusion with water, leaving behind the iron and manganese as monoxides in the form of a heavy, black sand. Small amounts of easily reducible metals such as tin and antimony (and tin is a constant constituent of the minerals) are completely removed in the metallic state, the metal usually alloying with the metal crucible. The aqueous extract is made slightly acid with hydrochloric acid and heated to boiling, when the hydrated pentoxides of columbium and tantalum separate out as a white precipitate. The precipitate is thoroughly washed by decantation with hot water.

The classic method for the decomposition of the minerals is fusion with acid potassium sulphate. For this purpose, the mineral is finely powdered and fused with three times its weight of the bisulphate; the fused mass is completely boiled out with water, when a residue of crude columbic and tantalic hydroxides is left. This is digested with ammonium sulphide for several days, in order to remove most of the tin and tungsten, which are always present. The residue is washed, boiled with a little dilute sulphuric acid, and again thoroughly washed with water.

The columbium and tantalum are separated by taking advantage of the different solubilities of the double potassium fluorides, K_2CbOF_5,H_2O and K_2TaF_7, which dissolve in about 12 and 200 times their weight of water respectively at the ordinary temperature. The hydroxides are dissolved in hot hydrofluoric acid, filtered from any mineral residue or potassium silicofluoride, the solution treated with enough potassium fluoride to form the double tantalum salt, and concentrated if necessary. On cooling, fine, characteristic, needle-shaped crystals of the tantalum salt separate out, and are washed with water. On evaporating the mother-liquor and wash-waters, more of the salt is obtained, which at last is mixed with scales of the columbium salt. The potassium tantalofluoride is purified from practically all impurities but a trace of silicofluoride by one or two crystallisations, mixed with its own weight of concentrated sulphuric acid and heated gradually to 400° until the hydrofluoric acid and most of the excess of sulphuric acid are expelled. The residue is then disintegrated by boiling with water, and thoroughly washed, first with water, and finally with dilute ammonium carbonate, until all the potassium and sulphuric acid have been removed. The pure tantalic hydroxide is then ignited if it is desired to form the pentoxide.

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[1] *Chem. News*, 1909, 99, 1, 25.

The filtrate from the tantalum salt is treated with a further quantity of potassium fluoride and concentrated, when, on cooling, the columbium salt, K_2CbOF_5,H_2O, separates out. The salt thus obtained contains a little tantalum. It is therefore heated to 200° for some hours and extracted with water, when a residue of potassium tantalum oxyfluoride is obtained and removed by filtration. The solution is evaporated to dryness and the baking at 200° and extraction with water are repeated until all the tantalum has been removed. From the purified columbium salt the silica-free hydroxide and oxide may be obtained as has already been described for tantalum.[1]

The oxides of columbium and tantalum obtained in the preceding manner usually contain small quantities of oxides of tin and tungsten. These may be removed by Rose's method of fusion with a mixture of sodium carbonate and sulphur, and extraction with water. The tin and tungsten pass into solution as thiostannate and tungstate, and the residual sodium columbate or tantalate is then washed with cold water, in which it is nearly insoluble, and fused with potassium bisulphate to recover the oxide. This treatment with sodium carbonate and sulphur may have to be repeated several times.

The columbic oxide still contains small amounts of oxide of titanium, and no satisfactory separation of this impurity is known which does not remove also a considerable proportion of the columbium. The simplest procedure is to crystallise the double fluoride, K_2CbF_7, from fairly concentrated hydrofluoric acid five or six times; this also eliminates tin and tungsten.[2]

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[1] Hall, *J. Amer. Chem. Soc.*, 1904, **26**, 1235; Hall and Smith, *ibid.*, 1905, **27**, 1369. See also Ruff and Schiller, *Zeit. anorg. Chem.*, 1911, **72**, 329.

[2] Balke and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1637; cf. Hall, *loc. cit.*; Hall and Smith, *loc. cit.*

Ruff and Schiller prefer to eliminate titanium by fractional distillation of the columbium pentachloride, the titanium chloride being much the more volatile.

431 Columbium was first obtained by Blomstrand,[1] by reducing the chloride in hydrogen, as a mirror-like deposit on the tube, but it was not certain whether this was the pure metal or a hydride. Roscoe[2] obtained it in the form of a steel-grey crust, by passing the vapour of the pure chloride together with hydrogen repeatedly through a red-hot tube; this was then more strongly heated in a porcelain tube, through which hydrogen was passed. The metal contained only 0·27 per cent. of hydrogen as well as a small quantity of chloride and oxide, the latter being derived from diffused air. It has been prepared in a somewhat impure condition as a metallic regulus by heating the pentoxide with carbon in the electric furnace,[3] and by reducing the pentoxide with the mixed metals of the cerite earths, the method being the same as that employed for vanadium (p. 948).[4] It can be obtained in the pure condition by preparing filaments of the oxide, CbO_2, by heating a mixture of the pentoxide and paraffin which has been pressed into threads, and then reducing this by passing through it an alternating current *in vacuo*. The regulus obtained by the aluminium reduction of the pentoxide may moreover be freed from aluminium by being heated *in vacuo* in an electric furnace.[5] The metal has the specific heat 0·071 and the density 8·4, and melts at about 1950°. The pure metal has a light grey colour, and is about as hard as wrought iron. It can be rolled into foil and then drawn into wire, and can be welded at a red heat. A regulus fused in a vacuum consists of crystals, apparently rhombic, several mm. in length. It combines only slowly with oxygen, even when it is strongly heated, and unites with hydrogen to form the hydride, CbH. This compound, which has also been obtained by Marignac, resembles the metal in its behaviour to acids, and burns when heated in the air.[6] Columbium is not dissolved by hydrochloric or nitric acid or aqua regia, even when heated, but when alloyed with other metals is attacked by acids. It is attacked by fused alkalis and fused oxidising agents, and combines with nitrogen at 1200°.

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[1] *J. pr. Chem.*, 1866, **97**, 37.

[2] *Mem. Manch. Phil. Soc.*, [3], 6, 186.

[3] Moissan, *Compt. rend.*, 1901, **133**, 20.

[4] Weiss and Aichel, *Annalen*, 1904, **337**, 380.

[5] Werner von Bolton, *Zeit. Elektrochem.*, 1907, **13**, 145.

[6] Krüss and Nilson, *Ber.*, 1887, **20**, 1691.

COMPOUNDS OF COLUMBIUM.

COLUMBIUM AND OXYGEN.

432 The two lower oxides of columbium are usually known as the dioxide, Cb_2O_2, and the tetroxide, Cb_2O_4, although they would more properly be termed the monoxide, CbO, and the dioxide, CbO_2.

Columbium Dioxide, CbO or Cb_2O_2, is formed when dry potassium columbium oxyfluoride is heated with sodium under a layer of potassium chloride over a gas blow-pipe, and was thought by Rose to be the metal. The fused mass is boiled with water, and the residue washed with water and afterwards with dilute alcohol. It then forms a white powder which on heating in the air oxidises with vivid incandescence. When gently warmed in chlorine gas, it burns with formation of oxychloride, and it dissolves in the moist state in hydrochloric acid with evolution of hydrogen. If the vapour of the oxychloride be passed over heated magnesium wire, the same compound is formed in crystals which belong probably to the regular system.

Columbium Tetroxide, CbO_2 or Cb_2O_4, is obtained as a heavy, black powder, which appears blue by reflected light, by heating the pentoxide very strongly in hydrogen or with metallic magnesium.[1] It is not attacked by acids, and burns in the air when heated to redness.

Columbium Pentoxide, Cb_2O_5.—The preparation of this oxide has been already described. It is a white, amorphous, infusible powder having a sp. gr. of 4·5 to 5·0, according to its method of preparation, and becomes yellow and crystalline when strongly heated. It may be obtained in prismatic crystals of sp. gr. 4·568 by fusion with boron trioxide or borax.

Columbic Acid or *Columbium Hydroxide*, $HCbO_3$, is obtained as already described on p. 977, and is also formed by the decomposition of the oxychloride or pentachloride in moist air or with water. It is a white powder which, when dried at 100°, retains varying quantities of water, and is converted into the pentoxide at a red heat with incandescence. It is only slightly soluble in hot hydrochloric acid, but the residue, after this treatment, can be dissolved in water. On the addition of zinc the solution becomes blue and a hydrated precipitate, probably of Cb_2O_4, separates out. The solution of columbic acid obtained by treatment with hydrochloric acid gives, on the other hand, a brown colour with zinc, and a brown oxide separates out which has the composition $Cb_3O_6(= CbO,2CbO_2)$. Columbic acid is easily soluble in caustic alkalis and their carbonates.

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[1] Smith and Maas, *Zeit. anorg. Chem.*, 1894, 7, 96.

Columbates.—The salts of columbic acid are termed columbates. Many of these salts were described by the early workers on columbium; but comparatively few were definite chemical individuals. The first definite sodium salt, $7Na_2O,6Cb_2O_5,32H_2O$, was prepared in 1905 by Bedford.[1] Since then the columbates have been carefully studied by Balke and Smith,[2] who have shown that several series of these salts can be obtained.

The 7 : 6 *series*, $7M^I_2O,6Cb_2O_5,xH_2O$.—The *sodium* salt of this series may be prepared by precipitating potassium columbium oxyfluoride in aqueous solution with three times its weight of caustic soda, washing the precipitate with cold water, and recrystallising from boiling water. The salt is not very soluble in hot, and almost insoluble in cold water. It may also be obtained by fusing columbium pentoxide with four parts of caustic soda or 3 parts of sodium carbonate, extracting most of the excess of alkali with cold water, and crystallising the residual sodium columbate. The salt is precipitated unchanged from its aqueous solution by the addition of alcohol, and from it, by double decomposition, the corresponding barium, silver, and zinc salts have been obtained. The potassium, cæsium, and lithium salts of this series are also known.

The 4 : 3 *series*, $4M^I_2O,3Cb_2O_5,xH_2O$.—The potassium, rubidium, and cæsium salts are known. The last two salts crystallise with $14H_2O$ and are isomorphous with each other and with the corresponding tantalates. The *potassium* salt crystallises with $16H_2O$ and is the easiest columbate of potassium to prepare, being obtained by fusing columbium pentoxide with twice its weight of potassium carbonate and crystallising the product from water (Marignac). Its aqueous solution yields the 7 : 6 salt when precipitated with alcohol.

The 1 : 1 *series*, M^I_2O,Cb_2O_5,xH_2O.—The sodium salt, $Na_2O,Cb_2O_5,7H_2O$, separates out when the mother-liquor from the crystallisation of the 7 : 6 salt is allowed to evaporate spontaneously, and may be prepared by slowly evaporating an aqueous solution of the 7 : 6 salt on the water-bath while an atmosphere of carbon dioxide is maintained above the solution.[3]

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[1] *J. Amer. Chem. Soc.*, 1905, 27, 1216.

[2] *Ibid.*, 1908, 30, 1637.

[3] Smith and van Haagen, *J. Amer. Chem. Soc.*, 1915, 37, 1783.

It is much more soluble than the 7 : 6 salt. It becomes anhydrous, *but is stable at a red heat.* From the aqueous solution, by double decomposition, the silver, magnesium, copper, cadmium, and aluminium salts have been prepared.

The 3 : 4 *series*, $3M'_2O,4Cb_2O_5,xH_2O$.—Only the rubidium salt is yet known.

Numerous crystalline columbates have been prepared by fusing the precipitated salts with the corresponding chlorides or with boric acid.[1]

Percolumbic Acid is formed as an amorphous, yellow powder when columbic acid is warmed with hydrogen peroxide, or when sulphuric acid is added to a solution of potassium percolumbate and the solution dialysed and evaporated. It has the composition of a hydrated percolumbic acid, $HCbO_4$, and is decomposed by dilute sulphuric acid only on warming, thus differing from other per-acids.[2] The percolumbic acid, $Cb(OH)_6$ or $Cb_2O_5,H_2O_2,5H_2O$, has also been prepared.[3]

Orthopercolumbates of the general formula M_3CbO_8, where M is a univalent metal, have been obtained by Balke and Smith;[4] these represent some of the most highly oxidised series of salts known. They are prepared by adding an excess of hydrogen peroxide to an aqueous solution of an alkali columbate, together with the corresponding alkali hydroxide, and precipitating with alcohol. The potassium, sodium, rubidium, and cæsium salts are anhydrous, white, crystalline solids, quite stable in air and in warm aqueous solution; they are decomposed, however, with liberation of oxygen, when the aqueous solutions are boiled. By double decomposition the following percolumbates have also been prepared:

$MgNaCbO_8,8H_2O$
$MgKCbO_8,7H_2O$
$MgRbCbO_8,7\frac{1}{2}H_2O$
$MgCsCbO_8,8H_2O$
$CaNaCbO_8,4H_2O$
$CaKCbO_8,4H_2O$

COLUMBIUM AND THE HALOGENS.

433 *Columbium Pentafluoride*, CbF_5, is prepared by treating the pentachloride with anhydrous hydrogen fluoride, and frac-

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[1] Larsson, *Zeit. anorg. Chem.*, 1896, **12**, 188. See also Holmquist, *Journ. Chem. Soc.*, 1898, **74**, ii, 388.

[2] Melikoff and Pissarjewsky, *Zeit. anorg. Chem.*, 1899, **20**, 340.

[3] Hall and Smith, *J. Amer. Chem. Soc.*, 1905, **27**, 1369.

[4] *J. Amer. Chem. Soc.*, 1908, **30**, 1637.

tionating out the product under reduced pressure. It is a colourless, crystalline solid of density 3·29, which melts at 75·5° and boils at 217—220°. It is rapidly decomposed by water, acids and alkalis, alcohol, and ether.[1]

Columbium Oxyfluoride, $CbOF_3$, is obtained by igniting a mixture of pentoxide and fluor-spar in a current of hydrogen chloride, in the form of small crystals closely resembling zirconium fluoride. It forms double salts with other metallic fluorides, of which those of potassium and ammonium have been investigated by Marignac, who prepared the following:

$2KF,CbOF_3,H_2O$	$2NH_4F,CbOF_3$
$3KF,CbOF_3$	$3NH_4F,CbOF_3$
$5KF,3CbOF_3,H_2O$	$5NH_4F,3CbOF_3,H_2O$
$4KF,3CbOF_3,2H_2O$	$NH_4F,CbOF_3$
$HF,3KF,CbOF_3$	$3NH_4F,CbOF_3,CbF_5$

These are crystallisable, and are formed by dissolving columbic acid in a larger or smaller quantity of hydrofluoric acid and adding the other fluorides in various proportions. The first salts of the two series, which Marignac terms normal salts, are those which are readily formed. The normal potassium salt is formed whenever the others are recrystallised, and is deposited in the form of thin, monoclinic scales soluble in 12 parts of water at the ordinary temperature. It is isomorphous with potassium tungsten oxyfluoride, $2KF,WO_2F_2$, and with potassium titanofluoride, K_2TiF_6. By dissolving the normal oxyfluoride in hot hydrofluoric acid *potassium columbifluoride*, K_2CbF_7, is formed, which is deposited in glistening, rhombic needles. The normal ammonium salt crystallises in rhombic tablets, and is isomorphous with ammonium tungsten oxyfluoride, $2NH_4F,WO_2F_2$.

Rubidium, cæsium, and thallous double fluorides of the type $2M^IF,CbOF_3$ are also known, and a sodium salt of the composition $3NaF,CbOF_3$. Like the potassium compound, the rubidium and cæsium salts are transformed into double fluorides of the type $2M^IF,CbF_5$ when crystallised from fairly concentrated hydrofluoric acid (Balke and Smith).

A double fluoride of the formula $2KF,3CbO_2F$ is gradually deposited in small quantity as a white powder when a solution of the normal potassium oxyfluoride is boiled for a considerable time:[1]

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[1] Ruff and Schiller, *Zeit. anorg. Chem.*, 1911, 72, 329.

$$3(2KF,CbOF_3) + 3H_2O = 2KF,3CbO_2F + 4KF + 6HF.$$

It is readily soluble in hydrofluoric acid.

Hydrogen peroxide converts the oxyfluoride into a peroxyfluoride, CbO_2F_3, which crystallises in yellowish plates.[2] The double sodium and rubidium peroxyfluorides have been similarly prepared (Balke and Smith).

Columbium Trichloride, $CbCl_3$, is obtained when the vapour of the pentachloride is slowly passed through a red hot glass tube, and when the oxide is heated with phosphorus pentachloride.[3] It either forms crystalline crusts which have the appearance of iodine, or is found crystallised in long needles which are dichroic. It is neither volatile nor deliquescent, and is not decomposed by water or ammonia, but is easily oxidised by nitric acid. When heated in the air it emits thick vapours, and when ignited in a current of carbon dioxide it forms columbium oxychloride, $CbOCl_3$, and carbon monoxide, a reaction which is not exhibited by any other metallic chloride (Roscoe).

Columbium Pentachloride, $CbCl_5$.—When an intimate mixture of columbium pentoxide and a large excess of sugar charcoal is heated in a current of chlorine perfectly free from air, yellow needles of the above compound are formed. The chloride is lso formed[4] when the pentoxide is heated in the vapour of ulphur monochloride and chlorine, or carbon tetrachloride and hlorine, or heated with carbon tetrachloride in a sealed tube t 200°; and, together with the oxychloride, when carbon etrachloride is passed over the heated pentoxide. It has a ensity of 2·75, melts at 194°, and boils at 240·5°, but begins to ublime at 125°. The yellow vapour has a specific gravity of ·6 (Deville and Troost), the formula requiring 9·38. The hloride is soluble in carbon tetrachloride, sulphur monochloride, hloroform, and alcohol. It dissolves in hydrochloric acid, orming a liquid which gelatinises on standing, and when diluted ith water or boiled almost all the columbic acid separates out.

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[1] Krüss and Nilson, *Ber.*, 1887, **20**, 1676.

[2] Piccini, *Zeit. anorg. Chem.*, 1892, **2**, 22.

[3] Bennington, *Chem. News*, 1897, **75**, 38.

[4] Smith, *J. Amer. Chem. Soc.*, 1898, **20**, 280; Hall and Smith, *ibid.*, 1905, **7**, 1369; Hall, *ibid.*, 1904, **26**, 1235; Ruff and Schiller, *Zeit. anorg. Chem.*, 11, **72**, 329.

Metallic zinc brought into the solution turns it a deep blue colour.

Columbium Oxychloride, or *Columbyl Chloride*, $CbOCl_3$, is formed by the direct union of the dioxide with chlorine, and also when a mixture of the pentoxide with a small quantity of carbon is heated in chlorine. It is best formed by heating the pentoxide in carbon tetrachloride vapour, and eliminating the pentachloride also produced by repeatedly distilling the mixture in a current of carbon dioxide over the pentoxide (Hall and Smith). It is a colourless, fibrous, crystalline mass, which volatilises without melting at about 400°, giving rise to a colourless vapour, the specific gravity of which was determined by Deville and Troost to be 7·88, theory requiring 7·48. When heated in carbon dioxide, and still more readily in hydrogen, it decomposes into pentoxide and pentachloride. It deliquesces on exposure to moist air, with formation of crystalline columbic acid, whilst when brought into contact with water it decomposes violently, forming amorphous columbic acid.

Double salts with various alkali chlorides and organic hydrochlorides have been prepared.[1]

When columbium oxide is heated in hydrogen chloride a hydroxychloride, $Cb_2O_4,3H_2O,HCl$, is formed which is volatile at a high temperature.[2] Hydrogen bromide yields an analogous compound.

Columbium Pentabromide, $CbBr_5$, obtained by the direct union of its elements,[3] closely resembles the chloride in properties. It is a purple-red mass, which forms deep garnet-red, prismatic crystals. It melts at about 150° and boils at 270°.

Columbium Oxybromide, $CbOBr_3$.—When a mixture of the pentoxide and double its weight of carbon is heated in bromine vapour a yellow, voluminous mass of the oxybromide is obtained, which sublimes without fusion in an inert atmosphere laden with bromine vapour, and even at comparatively low temperatures begins to decompose into the pentabromide and pentoxide (Barr).

HALIDE BASES OF COLUMBIUM.

Chlorocolumbium Chloride, $(Cb_6Cl_{12})Cl_2,7H_2O$, is obtained by heating columbium pentachloride with seven parts of 3 per cent.

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[1] Weinland and Storz, *Ber.*, 1906, 39, 3056; *Zeit. anorg. Chem.*, 1907, 54, 223.

[2] Smith and Maas, *Zeit. anorg. Chem.*, 1894, 7, 96.

[3] Barr, *J. Amer. Chem. Soc.*, 1908, 30, 1668.

sodium amalgam *in vacuo* at a temperature just sufficient to propagate the initial reaction through the mass, and subsequently heating for an hour to a temperature at which Jena glass begins to soften. The mass is cooled *in vacuo*, extracted with boiling water, the solution filtered from brown residue, and concentrated after the addition of a little hydrochloric acid. The yield is very small.

The chloride separates in small, shining crystals which appear black but give a green powder. It is very slightly soluble in cold and not very soluble in boiling water, the solution having an olive-green colour. It is not completely decomposed by ammonia even on long boiling, but boiling nitric acid decomposes it. The compound dissolves in concentrated alkalies to form a dark greenish-brown solution, from which, on adding excess of hydrochloric acid, a brown chloride, $Cb_6Cl_{14},9H_2O$, is obtained differing in constitution from the original chloride, although in composition it only differs in its water content. The brown chloride is re-converted into the green chloride when dissolved in water, the rate of change being rapid in boiling solution.

A solution of chlorocolumbium chloride, when treated with the theoretical amount of sodium hydroxide, gives a black, crystalline precipitate of *chlorocolumbium hydroxide*, $(Cb_6Cl_{12})(OH)_2,8H_2O$, soluble in both acids and alkalis. From its solution in hydrobromic acid, *chlorocolumbium bromide*, $(Cb_6Cl_{12})Br_2,7H_2O$, may be obtained in crystals which resemble the chloride but are more soluble in cold water.[1]

COLUMBIUM AND SULPHUR.

Columbium Sulphide.—When columbium pentoxide is heated to redness for a sufficient period in hydrogen sulphide it produces a brown product containing only columbium and sulphur. The product is black when a mixture of hydrogen sulphide and carbon disulphide is employed. No definite sulphide or oxysulphide has yet been obtained.[2]

COLUMBIUM AND NITROGEN.

435 *Columbium Nitride*, Cb_3N_5.—Metallic columbium forms a yellow nitride[3] when it is heated in nitrogen at 1,200°. A

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[1] Harned, *J. Amer. Chem. Soc.*, 1913, **35**, 1078.

[2] Biltz and Gonder, *Ber.*, 1907, **40**, 4963.

[3] Moissan, *Compt. rend.*, 1901, **133**, 20; Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, **355**, 58.

nitride also is presumably precipitated when dry ammonia gas is led into a solution of the pentachloride in carbon tetrachloride. It is separated from co-precipitated ammonium chloride by washing with water, and is decomposed by caustic alkali with the evolution of ammonia.[1] When columbium pentoxide is heated to whiteness in ammonia it loses the half of its oxygen, and forms a black powder containing nitrogen. If the oxychloride be treated with dry ammonia it becomes hot and turns yellow. This mass, when heated, gives off ammonium chloride, and a black powder remains behind, which, when melted with caustic potash, yields ammonia in large quantity, and on heating in the air burns with incandescence. It is not attacked either by boiling nitric acid or aqua regia, but dissolves readily in a mixture of hydrofluoric and nitric acids.

DETECTION AND ESTIMATION OF COLUMBIUM AND TANTALUM.

436 All columbates and tantalates are decomposed when the finely powdered minerals are fused with six times their weight of potassium hydroxide in a nickel or silver crucible, and on extracting with water potassium columbate and tantalate pass into solution. On acidifying the solution, columbic and tantalic acids separate out as a white, amorphous precipitate somewhat soluble in excess of acid. After treating the washed precipitate with ammonium sulphide to remove any tungstic acid, it may be tested for tantalum by dissolving in hydrofluoric acid, adding potassium fluoride, concentrating to a small volume, and allowing it to cool; characteristic needles of potassium fluotantalate separate out if tantalum is present. The filtrate is evaporated with excess of sulphuric acid to expel fluorine, cooled, diluted gradually with water, and treated with metallic zinc; if columbium is present a blue coloration is developed, due to a compound in which columbium is quadrivalent or trivalent.[2] For carrying out the colour test, Giles[3] recommends that the solution of potassium tantalate and columbate be acidified with an excess of either oxalic or phosphoric acid, which holds the acid earths in solution, and the hot solution treated with zinc dust, when a yellow, brown, or nearly black colour is developed, according to the amount of columbium present. Titanium, if present, gives

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[1] Hall and Smith, *J. Amer. Chem. Soc.*, 1905, **27**, 1369.

[2] See also Stähler, *Ber.*, 1914, **47**, 841.

[3] *Chem. News*, 1907, **95**, 37.

a similar colour when oxalic acid is used, but a lilac or violet tint if excess of phosphoric acid is present.

In a reducing flame, the microcosmic salt bead is coloured blue, violet, or brown by columbic acid, and after the addition of a little ferrous sulphate becomes red. No colour is produced by tantalic acid.

For the quantitative estimation of columbium and tantalum there are several methods available for decomposing the minerals. In some respects, the neatest method is to heat the finely divided mineral in a stream of sulphur monochloride vapour.[1] Columbium, tantalum, titanium, silicon, zirconium (?), tungsten, antimony (?), and most of the iron are thus removed as volatile chlorides and collected in a receiver charged with dilute nitric acid. This is treated with excess of ammonia, and hydrogen sulphide passed in until the separated sulphur has dissolved. Tungsten and antimony remain dissolved in the liquor, and, on filtering and washing, the mixed hydroxides of columbium, tantalum, titanium, silicon, and zirconium are obtained, together with ferrous sulphide. These are boiled with dilute sulphuric acid until the residual hydroxides of columbium, tantalum, titanium, and silicon are white. The small amount of the acid oxides which passes into the filtrate is reprecipitated by making the solution nearly neutral and boiling while a current of hydrogen sulphide passes through it to maintain the iron in the ferrous state. The titanium may now be removed from the mixed hydroxides by boiling for several hours with excess of salicylic acid solution, in which it dissolves,[2] forming a yellow solution.

The method that has been most frequently used in decomposing columbium-tantalum minerals is fusion with an excess of potassium hydrogen sulphate, the mixed acid oxides being separated as has already been described on p. 977. According to Simpson,[3] it is preferable to fuse with six parts of caustic potash, and extract with dilute hydrochloric acid, for opening up the minerals. In both these procedures, the presence of much titanium causes a considerable amount of the columbium and tantalum, particularly the former, to remain in solution.[4]

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[1] Hicks, *J. Amer. Chem. Soc.*, 1911, **33**, 1492.

[2] Dittrich and Freund, *Zeit. anorg. Chem.*, 1908, **56**, 344, 346; Muller, *J. Amer. Chem. Soc.*, 1911, **33**, 1506.

[3] *Bull. West Australia Geol. Soc.*, 1906, **23**, 71; *Chem. News*, 1909, **99**, 243.

[4] Noyes, *Tech. Quart.*, 1904, **17**, 218; Warren, *Amer. J. Sci.*, 1906, [4], **22**, 520; Crook and Johnstone, *Min. Mag.*, 1912, **16**, 244; Simpson, *loc. cit.* See also Schoeller and Powell, *Journ. Chem. Soc.*, 1921, **119**, 1927.

For the separate determination of the columbium and tantalum, it is simplest to weigh the mixed pentoxides and to determine the columbium by a volumetric process, based upon its reduction to a state corresponding approximately with the oxide Cb_2O_3 and titration with potassium permanganate. The reduction is effected by means of zinc in a sulphuric acid solution, succinic acid being added to maintain the columbium and tantalum in solution.[1]

The only gravimetric process known is the classic procedure of Marignac,[2] or one of its modifications.[3] The mixed hydroxides are dissolved in a small excess of hydrofluoric acid, and the hot solution mixed with one of potassium fluoride, using about two parts of the latter for each part of mixed oxides estimated to be present. The solution is concentrated to a small volume (10 cubic centimetres per gram of mineral under analysis) and set aside to cool. The bulk of the tantalum crystallises out as K_2TaF_7, which is washed several times with very little water. Filtrate and washings are concentrated to half the previous volume and cooled, when a further small crop of tantalum salt is obtained, washed, and examined with a lens for flat plates of the columbium salt, which must be removed, if present, by further washing. A third crop of crystals is similarly obtained, examined, and washed.

The final filtrate and washings, containing the columbium, is heated with excess of sulphuric acid to expel the fluorine, diluted with water, made slightly alkaline with ammonia, and heated to boiling. The columbic hydroxide is filtered, washed, ignited, and weighed as Cb_2O_5. The tantalum is similarly estimated in the combined crops of crystals, and the result increased by a small correction based upon the volumes of mother-liquor and wash-liquor obtained from the third crop of crystals. This correction is, of course, subtracted from the weight of Cb_2O_5.

The Atomic Weight of columbium was determined by Rose, Hermann, and Blomstrand, but their results are now of historical nterest only; and the first fairly accurate value, 94, was determined by Marignac in 1865, from analyses of K_2CbOF_5,H_2O. This value was unchallenged for over fifty years, when in 1908

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[1] Metzger and Taylor, *Zeit. anorg. Chem.*, 1909, 62, 382; *Chem. News*, 909, 100, 257, 270. See also Levy, *Analyst*, 1915, 40, 204.

[2] *Ann. Chim. Phys.*, 1866, [4], 8, 5, 49.

[3] Meimberg and Winzer, *Zeit. angew. Chem.*, 1913, 26, 157; Ruff and chiller, *Zeit. anorg. Chem.*, 1911, 72, 329.

Balke and Smith[1] determined the ratio $2CbCl_5 : Cb_2O_5$ by decomposing the chloride with water and igniting the columbic acid to oxide. Their results led to an atomic weight of 93·5. Subsequent work has shown that this method is not capable of giving results of the highest degree of accuracy, and a more trustworthy method was found by Smith and van Haagen,[2] who transformed sodium metacolumbate into sodium chloride by heating it in sulphur monochloride, and from the ratio $NaCbO_3 : NaCl$ obtained the value 93·13. The number at present (1922) adopted is accordingly 93·1.

TANTALUM. Ta = 181·5. At No. 73.

437 Metallic tantalum was first obtained in an impure state as a black powder by Berzelius, who heated potassium tantalofluoride with potassium. Moissan succeeded in preparing it as a fused regulus by reducing the pentoxide with carbon in the electric furnace, but the metal thus obtained contained carbon.[3] It was first obtained pure by von Bolton,[4] who prepared it by carrying out Berzelius's reaction, and then heating the compressed powder of the metal in an electric furnace in a vacuum, and also by passing a current through a filament of Ta_2O_4 in a vacuum, the oxygen being thus removed and a filament of the metal left.[5] It is also formed when the pentoxide is reduced by crude cerium (Weiss and Aichel), but the temperature is not sufficiently high to melt the tantalum, which is obtained as a silver-white, porous mass. It is manufactured by the action of sodium on sodium tantalofluoride, or by the electrolysis of fused potassium fluotantalate, followed by melting the crude metal *in vacuo*.[6]

The pure metal is silver-white in colour, has the sp. gr. 16·64 (von Bolton), melts at 2,850° (Pirani and Meyer), and has a normal atomic heat. Its compressibility is $0{\cdot}54 \times 10^{-6}$.[7] It is as hard as soft steel, and when hot can be rolled, hammered, and drawn into wire. The tensile strength of the metal is very high, a fine wire giving a breaking test of 93 kilograms per square mm.

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[1] *J. Amer. Chem. Soc.*, 1908, **30**, 1644.
[2] *Ibid.*, 1915, **37**, 1788.

[3] *Compt. rend.*, 1902, **134**, 211.

[4] *Zeit. Elektrochem.*, 1905, **11**, 45, 503, 722; German Patents, 152848; 152870; 153826; 155548; 161081; 163414; 171562.

[5] *Zeit. angew. Chem.*, 1906, **20**, 1, 537.
[6] *Mining Journal*, 1900, **80**, 363.

[7] Richards and Bartlett, *J. Amer. Chem. Soc.*, 1915, **37**, 470.

When heated in the air, thin wire burns, whilst more compact masses are oxidised superficially. The red hot powder decomposes water, and in the form of wire readily absorbs nitrogen and hydrogen, 740 volumes of the latter being taken up at a yellow heat. About three-quarters of this is lost in a vacuum at a red heat, but the remainder, which renders the metal brittle and increases its electrical resistance, is lost only on fusion.[1] Tantalum is not attacked by aqua regia nor by any single acid except hydrofluoric acid, which dissolves it much more readily when the metal is in contact with platinum. It is attacked also by fused alkalis. It combines with nitrogen at a high temperature, more readily with sulphur. Carbon appears to form with it a carbide and renders the metal brittle. Alloys with iron, tungsten, and molybdenum can be obtained.

The chief purpose for which metallic tantalum is employed is for the preparation of filaments for electric lamps. Wire of 0·05 mm. diameter is employed, and as the resistance is much less than that of a carbon filament, a much longer filament is used than in a carbon lamp. The lamps require only about half the energy needed by a carbon lamp of equal candle-power.

It has also been suggested to use tantalum in place of the more expensive platinum for crucibles, electrodes, etc., and for dental and surgical instruments.

COMPOUNDS OF TANTALUM.

TANTALUM AND OXYGEN.

438 *Tantalum Tetroxide*, Ta_2O_4 or TaO_2, is formed when the pentoxide is heated in a very small carbon crucible, exposed to the highest heat of a wind furnace, or reduced by metallic magnesium. It is a porous, dark-grey mass which scratches glass, and when rubbed on a hone has a steel-grey colour. It gives a dark-brown non-metallic powder, and is not attacked by acids, even by a mixture of hydrofluoric and nitric acids, but burns when heated, with formation of the pentoxide.

Tantalum Pentoxide, Ta_2O_5.—The preparation of this body has already been described (p. 977). It is a white, amorphous, infusible powder which when strongly heated becomes crystalline, and when ignited with boron trioxide or melted with microcosmic salt in a porcelain furnace is obtained in rhombic prisms. When gently heated it has a specific gravity of 7·35, which after exposure to a white heat rises to 8·7. The ignited pentoxide does not dissolve in any acid.

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[1] Piccini, *Zeit. Elektrochem.*, 1905, 11, 555.

Tantalic Acid or *Tantalum Hydroxide*, $HTaO_3$, is obtained in the form of a gelatinous mass when the chloride is quickly mixed with water. If, however, the same compound be exposed to moist air until it is decomposed, and then mixed with water containing ammonia, the hydroxide is obtained as a crystalline powder, which when dried at 100° possesses the above composition, and is converted with vivid incandescence into pentoxide when heated to low redness. The hydroxide obtained from the double fluoride by treatment with acid potassium sulphate does not exhibit this phenomenon. Tantalic acid dissolves in hydrofluoric acid, and, when freshly precipitated, in other acids.

The Tantalates.—The normal tantalates, to which class the tantalum minerals belong, are all insoluble in water. Besides these, others are known, derived from the unknown hydrate, hexatantalic acid, $H_8Ta_6O_{19}$, or $4H_2O,3Ta_2O_5$, of which only the compounds of the alkali metals are soluble in water.

Potassium Hexatantalate, $4K_2O,3Ta_2O_5,16H_2O$, is formed by dissolving the acid in caustic potash, and also by fusing the pentoxide with double its weight of caustic potash. The fused mass is dissolved in water and allowed to evaporate in a vacuum. Transparent, glistening, monoclinic crystals are thus obtained which dissolve in lukewarm water without decomposition. On boiling or evaporating in the air, salts containing more tantalum are formed. If it be repeatedly ignited with ammonium chloride and washed with water the normal salt, $KTaO_3$, is obtained.

Sodium Hexatantalate, $4Na_2O,3Ta_2O_5,25H_2O$, is obtained in a similar way to the potassium salt, a vivid incandescence occurring when the mixture is heated to redness. The fused mass is boiled out with water, and the solution either allowed to cool or, inasmuch as the salt is insoluble in caustic soda, poured on to the top of a strong solution of this substance. It crystallises in small, hexagonal tablets which dissolve at 13·5° in 493, and at 100° in 162 parts of water. It is not decomposed by boiling water, and if the aqueous solution be mixed with alcohol a precipitate of $NaTaO_3,H_2O$ is formed, and this becomes anhydrous on ignition. The anhydrous salt is also formed by the ignition of the hexatantalate.

Rubidium and *Cæsium* hexatantalates crystallise with $14H_2O$ and are isomorphous with the corresponding columbates.[1]

When tantalum pentoxide is strongly ignited with the chlorides of calcium, magnesium, and other metals, crystalline tantalates of these metals are obtained.[2]

Pertantalic Acid.—When a large excess of hydrogen peroxide is added to a solution of potassium hexatantalate and potassium hydroxide and the liquid mixed with an equal volume of alcohol, a white, crystalline precipitate of *potassium pertantalate*, K_3TaO_8, is obtained.[3] This salt is decomposed by sulphuric acid with formation of a white precipitate of hydrated *pertantalic acid*, $HTaO_4$. This substance is more stable than percolumbic acid, but yields hydrogen peroxide when heated for some time at 100° with dilute sulphuric acid, and evolves ozonised oxygen when treated with concentrated sulphuric acid. The salts appear to be derived from the unknown ortho-form of this acid, which would have the formula $(HO{\cdot}O)_3TaO_2$. The sodium, rubidium, and cæsium salts are also known.[4]

TANTALUM AND THE HALOGENS.

439 *Tantalum Pentafluoride*, TaF_5, is prepared exactly like the columbium compound, which it closely resembles in properties. It forms large, colourless prisms of density 4·744, melts at 96·8°, and boils at 229·2 to 229·5°.[5]

Potassium Tantalofluoride, K_2TaF_7.—The mode of preparing this salt has been already described (p. 977). It forms small, rhombic needles which readily melt, but it does not decompose when ignited even to whiteness in a platinum vessel. It is easily soluble in hot, though sparingly so in cold water (about 1 part in 200 parts of water). When the solution is boiled decomposition takes place rapidly, a white powder of the *oxyfluoride*, $K_4Ta_4O_5F_{14} = 4KF,2TaF_5,Ta_2O_5$, separating out. Hence the salt should be crystallised from dilute hydrofluoric acid.

Sodium Tantalofluoride, Na_2TaF_7,H_2O, is obtained in a similar manner to the potassium salt, or by dissolving sodium hexatantalate in hydrofluoric acid. On evaporation, indistinct crystals of Na_3TaF_8 separate out, and then eight-sided rhombic tablets of the above salt, which lose their water below 100°.

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[1] Balke and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1637.

[2] Joly, *Compt. rend.*, 1875, **81**, 266, 1266.

[3] Melikoff and Pissarjewsky, *Zeit. anorg. Chem.*, 1899, **20**, 340.

[4] Balke, *J. Amer. Chem. Soc.*, 1905, **27**, 1140; Balke and Smith, *ibid.*, 1908, **30**, 1637.

[5] Ruff and Schiller, *Zeit. anorg. Chem.*, 1911, **72**, 329.

Ammonium, rubidium, and cæsium salts of the type $2M^IF,TaF_5$ are also known, as well as the corresponding zinc and copper salts.[1] *Lithium*, sodium, and cæsium double fluorides of the type M^IF,TaF_5 have also been described.[2] Hydrogen peroxide converts the potassium and rubidium salts, $M^I_2TaF_7$, into the *peroxyfluorides*, $2M^IF,TaO_2F_3,H_2O$, which crystallise in colourless plates (Piccini, Balke and Smith).

Tantalum Pentachloride, $TaCl_5$, is obtained by heating an intimate mixture of the pentoxide and carbon in a current of chlorine, and is also formed when the pentoxide is heated with phosphorus pentachloride. It is best prepared by heating the pentoxide in a current of chlorine mixed with either sulphur monochloride or carbon tetrachloride.[3] It forms light yellow needles and prisms of density 3·68, which melt at 211° and boil at 242°, but begin to volatilise at so low a temperature as 144°, and may be readily sublimed in a current of carbon dioxide or chlorine. The specific gravity of the vapour, according to Deville and Troost, is 12·8, the calculated density being 12·42. It fumes in the air, and is converted into tantalic acid by water. It is reduced by aluminium in presence of aluminium chloride to a mixture of lower chlorides.[4]

Tantalum Pentabromide, $TaBr_5$, is prepared by heating a mixture of equal parts of the pentoxide and carbon in a current of bromine vapour. It is best purified by sublimation *in vacuo*.[5] It forms yellow, elongated lamellæ, which melt at 240° to a ruby-red liquid and boils at 320°. The vapour resembles chlorine in colour. It fumes in air and is rapidly decomposed by water. The bromide may be sublimed in an atmosphere of hydrogen, but at high temperatures partial reduction to the metal takes place; also, traces of green bromotantalum bromide are produced. When the bromide has been exposed to traces of moisture and is then sublimed *in vacuo*, tantalum oxybromide, $TaOBr_3$, is left as a small residue.

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[1] Marignac, *Ann. Chim. Phys.*, 1866, [4], 9. 247; Balke, *loc. cit.*

[2] Balke, *J. Amer. Chem. Soc.*, 1905, 27, 1140.

[3] Hall and Smith, *ibid.*, 1905, 27, 1369; Balke, *ibid.*, 1910, 32, 1127; Ruff and Schiller, *Zeit. anorg. Chem.*, 1911, 72, 329.

[4] Ruff and Thomas, *Ber.*, 1922, 55, [*B*], 1466.

[5] van Haagen, *J. Amer. Chem. Soc.*, 1910, 32, 729; Smith and Chapin, *ibid.*, 1911, 33, 1497.

Tantalum Pentaiodide, TaI_5, is prepared by distilling the pentabromide slowly several times in a brisk current of dry hydrogen iodide.[1] It sublimes in nearly black lamellæ, and fuses to a dark brown liquid which gives a vapour resembling bromine. The iodide closely resembles the chloride and bromide in properties.

HALIDE BASES OF TANTALUM.

Bromotantalum Bromide, $(Ta_6Br_{12})Br_2,7H_2O$, is prepared by heating tantalum pentabromide with four parts of 3 per cent. sodium amalgam in vacuo, the temperature being gradually raised to a red heat. The mass is cooled *in vacuo*, extracted with boiling dilute hydrobromic acid, filtered from the residual brown powder (a lower oxide of tantalum), and concentrated on a water-bath.

The bromide forms small dark green crystals which are soluble in water, forming an emerald green solution, a one per cent. solution of which appears opaque in a half-inch layer. It is stable at 100°. From boiling- and freezing-point determinations, it has been found that the salt dissociates in solution into three ions, so that the formula should be written $(Ta_6Br_{12})Br_2,7H_2O$, the group Ta_6Br_{12} behaving as a divalent radicle of considerable stability. In cold aqueous solution, silver nitrate precipitates only one-seventh of the total bromine.

By the interaction of the bromide with the theoretical amount of caustic soda, a green, crystalline precipitate of *bromotantalum hydroxide*, $(Ta_6Br_{12})(OH)_2,10H_2O$, is obtained, nearly insoluble in water. Solution of the hydroxide in hydrochloric and hydriodic acids leads to the formation of *bromotantalum chloride*, $(Ta_6Br_{12})Cl_2,7H_2O$, and *bromotantalum iodide*, $(Ta_6Br_{12})I_2,7H_2O$, respectively. The former may also be obtained from the bromide by evaporation with hydrochloric acid, and in cold aqueous solution it gives a precipitate of silver chloride, free from bromide, upon the addition of silver nitrate.[2]

Chlorotantalum Chloride, $(Ta_6Cl_{12})Cl_2,7H_2O$, is obtained by reducing tantalum pentachloride with sodium amalgam, as in the case of the bromotantalum bromide, which it resembles in appearance and properties (Chapin). This salt was first obtained, in very small amount, by Chabrié, who mistook it for a dichloride, $TaCl_2,2H_2O$.[1]

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[1] van Haagen, *loc. cit.*

[2] Chapin, *J. Amer. Chem. Soc.*, 1910, 32. 323.

TANTALUM AND SULPHUR.

440 *Tantalum Disulphide,* TaS_2, is produced in the crystalline form when the pentoxide is heated to 900° in a stream of hydrogen sulphide and carbon disulphide. It begins to sublime at 1200° and is stable at 1300°.[2]

TANTALUM AND NITROGEN.

441 When tantalum chloride is heated in ammonia gas to a temperature not above the point of volatilisation of the ammonium chloride which is formed, an amorphous, yellowish-red mass of varying composition is obtained. If this is powdered and heated to redness in a stream of ammonia it is converted into a bright red, amorphous powder having the composition Ta_3N_5. When this is raised to a full white heat in an atmosphere of ammonia, an amorphous, black powder of *tantalum nitride,* TaN, is produced which exhibits a metallic lustre on burnishing. H. Rose, who first obtained this compound, believed it to be the metal.[3] The nitride, Ta_3N_5, is also obtained when metallic tantalum is heated in nitrogen gas to a temperature of 1000.°

TANTALUM AND CARBON.

Tantalum Carbide.—When 6 parts of Ta_2O_5, 1 part of sodium carbonate, and 1 part of charcoal are heated to a temperature of about 1480°, tantalum carbide, TaC, is produced in the form of fine needles.[4]

DETECTION AND ESTIMATION OF TANTALUM.

442 The detection and estimation of tantalum have already been discussed under columbium (p. 987).

The Atomic Weight was determined by Marignac,[5] who analysed the potassium and ammonium tantalofluorides and obtained the number 183. For forty years the accepted value for the atomic weight rested upon the analyses made by Marignac, which were by no means concordant; then, in 1906, by direct conversion of the metal into the pentoxide Hinrichsen and Sahlbom[1] obtained the number 181. Later, by converting the pentachloride into the oxide, Balke[2] found 181·52, and Chapin and Smith found 181·8 by transforming the pentabromide into the oxide.[3] The number at present (1922) adopted is 181·5, but the work of Sears and Balke[4] indicates that this result is probably in need of revision.

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[1] *Compt. rend.*, 1907, **144**, 804.

[2] Biltz and Kircher, *Ber.*, 1910, **43**, 1636.

[3] Muthmann, Weiss, and Riedelbauch, *Annalen*, 1907, **355**, 58.

[4] Joly, *Compt. rend.*, 1876, **82**, 1195.

[5] *Ann. Chim. Phys.*, 1866, [4] **9**, 251.

ANTIMONY (STIBIUM). Sb = 120·2. At. No. 51.

443 This metal occurs in nature chiefly as stibnite, antimonite, or antimony sulphide, Sb_2S_3, a mineral which was known in very early times, having been long employed, as indeed is yet the case, by women in the East for painting the eyebrows. In St. Jerome's translation of the Hebrew of Ezekiel xxiii. 40, we read "circumlinisti stibio oculos tuos"; and in the Second Book of Kings ix. 30, we find, "Porro Jezebel introitu eius audito depixit oculos suos stibio." Of this latter passage Cheyne and Drover give as the translation of the Hebrew, "set her eyes in paint (literally antimony)."

The name for this mineral in Hebrew and Arabic is "Kohl," and this word passed as "alcool" or "alkohol" into other languages; thus in the Spanish translation of the Bible the above passage from Ezekiel is thus rendered, "Alcoholaste tus ojos." In the middle ages the word alcohol indicated any fine powder; it was only at a later period that it was employed to mean spirits of wine. Dioscorides calls this metal *στίμμι*, and mentions that it is also known by other terms, such as *πλατυόφθαλμον*, the eye-expander, *γυναικεῖον*, belonging to womankind, etc. Pliny, on the other hand, terms it *stibium*. The Latin Geber, who also was acquainted with this substance, termed it *antimonium*, and up to the time of Lavoisier both these words were made use of to signify sulphide of antimony. The German name was *spiessglas*, afterwards changed to *spiessglanz*. As already mentioned (Vol. I., p. 9), the works attributed to "Basil Valentine," which have hitherto been regarded as the earliest known records concerning antimony and its derivatives, were shown by Schorlemmer to be forgeries dating from about 1600.[1] There is no doubt, however, that the iatro-chemists, from the time of Paracelsus, were acquainted with many antimonial preparations, and numerous references to these are scattered throughout the chemical literature of those times. The statements of "Basil Valentine" may still serve to show the condition of knowledge concerning antimony in 1600. He remarks in his *Triumphal Car of Antimony*: "In order, as is most proper, that I may say something about the name of the material, it should be understood that this material was long known to the Arabians, and from ancient time was termed by them *asinat*. The Chaldeans entitled it *stibium*, and in the Latin tongue it has been called *antimonium*[2] up to the latest times, and in our own German mother tongue the same material has been foolishly called spiessglas for this reason, that this material can be fluxed and a glass made from it."

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[1] *Ber.*, 1906, **39**, 2600.

[2] *Ibid.*, 1911, **39**, 1497.

[3] *J. Amer. Chem. Soc.*, 1910, **32**, 1127.

[4] *Ibid.*, 1915, **37**, 833; 1917, **39**, 1582.

Dioscorides mentions that in order to roast the crude antimony it must be heated in a current of air until it burns, for if more strongly ignited, it melts like lead. This passage has given rise to the supposition that the author was acquainted with metallic antimony, and that this is probably the case is shown by the fact that an old Chaldean vase analysed by Berthelot consisted of pure antimony.[3] Antimony was confounded with bismuth by some chemists, such as Libavius, even so late as the sixteenth century.

The preparation of the metal was described by "Basil Valentine," who in his *Wiederholung des Grossen Steins der uralten Weisen* terms it *spiessglas rex* and also *plumbum antimonii*. It has already been stated that the alchemists considered each semi-metal to be a variation of a true metal.

444 Antimony occurs in many other minerals besides stibnite. The metal is found, though not frequently, in the native state, and also as arseniferous antimony or allemontite (AsSb). Antimony also occurs as the trisulphide, Sb_2S_3, combined with basic sulphides, and in these thioantimonites a portion of the antimony is usually replaced by arsenic. Amongst such compounds are berthierite, FeS,Sb_2S_3; wolfsbergite or antimonial copper, Cu_2S,Sb_2S_3;

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[1] MSS. deposited in the library of the University of Manchester. See also Pierce, *Science*, 1898, 8, 169, who comes to the same conclusion, chiefly from a study of the contents of Basil Valentine's works.

[2] The story of the accidental poisoning of certain monks by spiessglas having given rise to the name of the metal (antimoine) is on the face of it improbable, and must, as Kopp remarks, have been invented by a Frenchman, whereas Valentine wrote in German!

[3] *Compt. rend.*, 1887, **104**, 265.

boulangerite, $5PbS,Sb_2S_3$; jamesonite $2PbS,Sb_2S_3$; bournonite, $2PbS,Cu_2S,Sb_2S_3$; pyrargyrite or red silver ore, $3Ag_2S,Sb_2S_3$, etc. In addition to these we have dyscrasite or antimonial silver, Ag_2Sb, breithauptite or antimonial nickel, NiSb, ullmannite or nickeliferous grey antimony, NiSbS; valentinite or antimony oxide, Sb_2O_3; cervanite or antimony ochre, Sb_2O_4 and stiblite, Sb_2O_4,H_2O. Antimony is also found in small quantity in iron ores, ferruginous waters, in the coal formation, and in river sand.

445 *Preparation of Metallic Antimony.*[1]—The preparation of the metal from the sulphide is a very simple operation. In order to free the ore from quartz or other earthy admixture, the mineral is either melted in vertical cylinders which have a hole at the bottom out of which the molten sulphide drops, or the preliminary fusion is carried on in reverberatory furnaces. The purified sulphide is then fused with metallic iron, or roasted to convert it into oxide, which is reduced with carbon or crude tartar. "Basil Valentine" describes both of these methods in his account of the preparation of the philosopher's stone; he states: "Antimonium is a master in medicine, and from it by means of cream of tartar and salt a King (regulus) is made, steel-iron being added to the spiessglas during fusion. Thus by an artifice a wonderful star is obtained which the learned before my time have termed the philosophical signet star." In the *Triumphal Car of Antimony* he gives the following receipt: "Take good Hungarian spiessglas and with the same quantity of crude tartar, and half as much saltpetre; rub these small and let them fuse well in a wind furnace; afterwards pour out into a mould and allow to cool when a regulus is found."

In the English process, three operations are used for the production of the best star-antimony. The first of these is termed "singling"; in this 40 parts of the liquated sulphide are mixed with about 18 parts of thin scrap iron and 4 parts of salt; and this is then melted in plumbago crucibles, when metallic antimony and iron sulphide are formed. The fusion lasts about an hour and a half, and when complete the charge is poured into conical moulds. The crude metal is then separated from the slag, consisting chiefly of sulphide of iron, which floats on the surface, and it is again melted in the second process of "doubling," with an addition of a small quantity of liquated stibnite, sodium sulphate or salt, and slag obtained in the following operation. The charge for each pot is 80 lb. of crude antimony, 7 lb. of liquated stibnite, 2 lb. of salt-cake, and 2 lb. of slag, and the fusion lasts about an hour and a half. The metal is cast in moulds, allowed to cool, and broken into small pieces ready for the third process, termed "melting for star-metal." For this purpose 2 parts of pearl-ash and 5 parts of slag from a previous operation of the same kind are added to 60 parts of metal, and the fusion is repeated. The molten metal is then poured into square moulds in which it is allowed to cool slowly, the surface being at the same time completely covered with slag in order that it may attain the peculiar crystalline structure which is required in commerce.

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[1] For full particulars, see *Antimony*, by C. Y. Wang (C. Griffin & Co., 1909).

In the roast and reduction method for the extraction of antimony, two distinct processes are in use; in the first, the sulphide ore is roasted to the stable tetroxide, generally in reverberatory or muffle furnaces at a temperature of about 350°. In the second process the volatile trioxide is formed by restricting the amount of air admitted, and working at a higher temperature, and is condensed in pipes and chambers. This process has several advantages, for low grade ores may be treated with success, arsenic oxide may be separated owing to its greater volatility, and in the case of ores containing precious metals, these may be extracted from the residues.

The oxide of antimony obtained by either process may be reduced to the metallic state by fusion with coal or charcoal, together with alkaline fluxes such as potash, soda, etc., in small reverberatory furnaces or crucibles.

It has been stated already that "Basil Valentine" was acquainted with the crystalline surface exhibited by pure antimony, but he specially mentions that the regulus which is not starred possesses exactly the same composition as that which presents this peculiarity. He, as well as some of his contemporaries, believed that the stellated surface was produced only when iron was employed in the preparation, whilst other chemists taught that the preparation of the stellated antimony was connected with a favourable conjunction of the stars. Indeed this latter opinion was generally held until the time of Boyle, who, however, discredited both views.

In his essay *On the Unsuccessfulness of Experiments*, Boyle[1] says: "And it may perhaps also be from some diversity either in antimonies or irons, that eminent chemists have (as we have observed) often failed in their endeavours to make the starry regulus of *Mars* and antimony. Insomuch that divers artists fondly believe and teach (what our experience will not permit us to allow) that there is a certain respect to times and constellations requisite to the producing of this (I confess admirable) body. Upon this subject I must not omit to tell you that a while since an industrious acquaintance of ours was working on an antimony, which unawares to him, was, as we then supposed, of so peculiar a nature, that making a regulus of it alone without iron, the common way (for his manner of operation I inquired of him), he found, to his wonder, and showed me his regulus adorned with a more conspicuous star than I have seen in several stellate reguluses of both antimony and *Mars*." Lemery, in his *Cours de Chymie*, published in 1675, also argues strongly against the supposition that the planet Mars has anything to do with the formation of the stellated surface.

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[1] *Opera*, ed. 1772, 1, 325.

Commercial antimony often contains traces of silver, gold, arsenic, iron, lead, copper, and frequently some sulphur. In order to prepare the pure metal, 16 parts of the commercial metal are fused with 2 parts of sodium carbonate and 1 part of sulphide of antimony for an hour; on cooling, the regulus is separated from the slag, and melted again for an hour with $1\frac{1}{2}$ parts of sodium carbonate, and the operation again performed with 1 part of this salt,[1] a small quantity of nitre being added from time to time.[2] The whole of the arsenic is thus separated, provided that a sufficient quantity of iron be originally present in the metal; should this not be the case, it is necessary to add about 2 per cent. of iron sulphide.[3]

Another method for preparing pure antimony is as follows.[4] Redistilled antimony trichloride or pentachloride is dissolved in concentrated hydrochloric acid, chlorine passed into the solution until it becomes greenish-yellow, and hydrogen chlorine then conducted into it, when chloroantimonic acid crystallises out. This is purified by recrystallisation, decomposed by hot water to antimonic acid, and the latter reduced to the metal by fusion with potassium cyanide.

446 *Properties.*—Antimony is a lustrous silver-white metal, which when slowly cooled exhibits a coarsely laminated crystalline fracture. When quickly cooled, on the other hand, the fracture is granular. It crystallises in obtuse rhombohedra, which can scarcely be distinguished from cubes, and has a specific

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[1] Liebig, *Annalen*, 1857, **104**, 223.

[2] *Ibid.*, 1835, **19**, 22.

[3] Bensch, *ibid.*, 1847, **63**, 273. *See also* Meyer, *ibid.*, 1848, **66**, 238.

[4] Groschuff, *Zeit. anorg. Chem.*, 1918, **103**, 164.

gravity of 6·71 to 6·86. Native antimony occurs in scaly masses, usually containing silver, iron, and arsenic. Its most important localities are at Sahl in Sweden, Andreasberg in the Harz, Przibram in Bohemia, in the Dauphiny, in Canada, the United States, Mexico, Chili, Sarawak, in Borneo and Queensland. Native antimony has a specific gravity of from 6·5 to 7. The metal has a normal atomic heat at ordinary temperatures; at 80° (Abs.) its atomic heat is 5·19.[1]

Antimony is hard, and so brittle that it can be powdered; it melts at 630·3°,[2] and volatilises at a bright red heat in the air, or in a current of a gas, but not when fused under a layer of common salt. It may be distilled in a current of hydrogen at a white heat. The vapour density of antimony is 10·74 at 1572°, and 9·78 at 1640° (Meyer and Biltz),[3] numbers which are intermediate between those required for the molecular formulæ Sb_2 and Sb. It does not undergo any alteration on exposure to the air at the ordinary temperature; on heating it burns to form the oxide, and when heated on charcoal before the blowpipe, the oxide is evolved in thick, white fumes, and a portion of it is deposited as a white incrustation on the charcoal. If the blast of air be stopped the globule of molten metal begins to glow, and is seen to be covered with a crystalline network of needles of oxide, and when the globule is thrown from some height on to a piece of paper, the edges of which are turned up, it breaks into many smaller globules which burn with a very bright flame. Neither cold water nor dilute sulphuric acid acts upon the metal at the ordinary temperature, but at a red heat it decomposes steam with formation of oxide. Nitric acid converts it into a white powder, the composition of which depends on the strength of the acid, nitrogen peroxide being evolved and no ammonia formed.[4] Pure antimony does not dissolve in strong hydrochloric acid in the absence of oxygen,[5] but the ordinary metal is easily dissolved by hot hydrochloric acid as well as by cold aqua regia, and when heated with concentrated sulphuric acid is converted into antimony sulphate. Antimony combines directly with the elements of the chlorine group, with those of the sulphur group, and with phosphorus and arsenic.

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[1] Günther, *Ann. Physik*, 1920, [4], **63**, 475.

[2] Holborn and Day, *ibid.*, 1900, [4], **2**, 505. See also Heycock and Neville, *Journ. Chem. Soc.*, 1895, **67**, 186; Groschuff, *Zeit. anorg. Chem.*, 1918, **103**, 164.

[3] *Ber.*, 1899, **22**, 725. See also *Annalen*, 1887, **240**, 317.

[4] Montemartini, *Gazz.*, 1892, **22**, 384.

[5] Ditte and Metzner, *Compt. rend.*, 1892, **115**, 936.

Colloidal solutions of antimony may be obtained by acting upon a tartaric acid solution of potassium antimonate with potassium hyposulphite.[1]

Allotropic Modifications of Antimony.—The grey, metallic form of antimony described above is the stable modification, although Cohen regards it as a mixture of several allotropic forms the relative proportions of which depend upon the previous history of the metal.[2] Unstable yellow and black modifications, corresponding with the unstable yellow and stable grey forms of arsenic (Vol. I., p. 691) also exist.[3] The yellow form is obtained by the action of oxygen on liquid stibine at −90°, and by the action of chlorine on stibine, both dissolved in liquid ethane at −100°. It is amorphous, appears to dissolve slightly in carbon disulphide, and passes very readily, when the temperature rises above − 90°, into the black variety. The latter can also be prepared by the rapid cooling of antimony vapour, and by the action of oxygen on liquid stibine at −40°. It is an amorphous black powder, has the specific gravity 5·3, oxidises spontaneously in the air, sometimes taking fire, and passes when heated into the stable metallic form with evolution of heat.

Explosive or Electrolytic Antimony.—This peculiar substance, discovered by Gore,[4] is obtained by electrolysis of an acid solution of antimony trichloride having a specific gravity of 1·35, or of a solution obtained by dissolving the trioxide in from five to six times its weight of hydrochloric acid of specific gravity 1·12, metallic antimony being, in each case, used as the positive, and copper or platinum as the negative pole. The latter becomes covered with a grey, lustrous, metallic coating, having an amorphous fracture and a specific gravity of 5·78. It contains from 4·8 to 7·9 per cent. of antimony chloride, together with a small quantity of free hydrochloric acid. When scratched with a metallic point or touched with a red hot wire it decomposes with evolution of heat and liberation of the chloride, and when heated to 200° it flies into powder with a loud explosion. If it be preserved under cold water it does not immediately undergo any alteration, but when heated to 75° it decomposes with a hissing sound; hydrochloric acid is found in solution, and the water becomes turbid owing to the formation of basic antimony chloride. Similar products are obtained by the electrolysis of acid solutions of the bromide and iodide (Gore), but not of the fluoride.

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[1] See Gutbier and Kräutle, *Kolloid Zeit.*, 1917, **20**, 194.

[2] Cohen and van den Bosch, *Zeit. physikal. Chem.*, 1915, **89**, 757.

[3] Stock and Guttmann, *Ber.*, 1904, **37**, 885; Stock and Siebert, *ibid.*, 1905, **38**, 3837.

[4] *Phil. Trans.*, 1858, **148**, 185; 1859, **149**, 797; 1862, **152**, 323; Pfeifer, *Annalen*, 1881, **209**, 61.

This remarkable substance is probably a solid solution of an antimony halogen compound in an allotropic form of antimony, and the explosion consists in the sudden transformation of the latter into the stable metallic form, the heat evolved amounting to 20 cal. per gram; the same change goes on slowly when the explosive material is preserved.[1] This form is possibly identical with the black amorphous form described above, but the identity has not been definitely proved.

Uses.—Antimony is employed for the preparation of tartar emetic, and of other products used in pharmacy and in many processes of calico printing and dyeing. Its alloys are also largely used in the arts. When antimony is precipitated by zinc from a solution of the trichloride, the metal is obtained in a finely pulverulent state, as *antimony black*; this is employed for the purpose of imparting to the surface of gypsum figures and other objects the appearance of iron or steel.

447 *Antimony Alloys.*—"Basil Valentine" mentions that antimony is valuable for the preparation of medicines, and that it is likewise employed for other purposes, such as for the preparation of printers' type. He adds that under certain favourable conjunctions of the planets alloys are made of antimony, and from these seals and amulets are cast, which are said to possess special virtues. These same alloys can, according to Valentine, be cast in the same way to form both bells and mirrors.

English type metal is an alloy of lead, antimony, and tin. A small percentage of copper is sometimes added, but is found of little practical value. The value of antimony in these alloys is that it imparts to them hardness, and gives them the property of expanding in the act of solidification so necessary in order to obtain an accurate cast of the letter. The tin gives toughness and coherence to the metal. The following are analyses of English type metal:

	I.	II.	III.	IV.	V.	VI.	VII.
Lead	50	60·0	61·3	96·2	85·7	83·5	80·0
Antimony . .	25	30·0	18·8	19·5	14·3	13·5	15·0
Tin	25	10·0	20·2	9·1	—	3·0	5·0
Copper . . .	—	—	—	1·7	—	—	—

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[1] Cohen and Ringer, *Zeit. physikal. Chem.*, 1904, **47**, 1; Cohen, Collins, and Strengers, *ibid.*, 1905, **50**, 291; Cohen and Strengers, *ibid.*, 1905, **52**, 129.

No. I is supposed to give the best results for high class work, but owing to the high price of tin No. II. is generally used. No. V is used for stereotype plates, No. VI is linotype metal, and No. VII. monotype metal.

Britannia Metal and *Pewter*.—This silver-white metal is largely used for the preparation of spoons, cups, and other articles. It consists mainly of tin and antimony, but frequently contains other metals, as is shown by the following analyses :

	Britannia Metal.		Plate Pewter.	Ashbury Metal.	Metal Argentum.
Tin	85·7	81·9	89·3	77·8	85·5
Antimony	10·4	16·2	7·1	19·4	14·5
Copper	1·0	—	1·8	—	—
Zinc	2·9	1·9	—	2·8	—
Bismuth	—	—	1·8	—	—

White or *anti-friction metal* is chiefly used for lining the brasses of various parts of locomotive engines and for the solid bushes for the coupling-rods. Several alloys are used for this purpose, as is seen by the following analyses :

	I.	II.	III.
Copper	5·3	1·5	—
Antimony	10·5	13·0	20
Tin	84·2	45·5	20
Lead	—	44·0	60

The alloy employed for the manufacture of ship's nails consists of 3 parts of tin, 2 of lead, and 1 of antimony.

Brass articles can be covered with a fine, lustrous coating of antimony by dipping them into a hot solution of 1 part of tartar emetic, 1 of tartaric acid, and 3 of water, to which 3 or 4 parts of hydrochloric acid and as much powdered antimony have been added.

Antimony forms a beautiful purple alloy with copper which has the composition Cu_2Sb, and is known as Regulus of Venus. With tellurium it forms a continuous series of mixed crystals.[1]

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[1] Dreifuss, *Zeit. Elektrochem.*, 1022, 28, 100, 224.

COMPOUNDS OF ANTIMONY.

ANTIMONY AND HYDROGEN.

448 *Antimony Hydride* or *Stibine*, SbH_3.—This substance was first prepared in 1837 by Lewis Thompson,[1] and also independently by Pfaff[2] and other chemists. It is formed when nascent hydrogen is brought into contact with a soluble antimony compound, or when an alloy of potassium or sodium with antimony is decomposed by water, or an alloy of zinc and antimony by dilute hydrochloric or sulphuric acid. It is also formed when antimony oxide is added to an acid solution which is evolving hydrogen. All these methods, however, furnish a gas which is largely mixed with free hydrogen,[3] and the preparation of pure stibine is a matter of some difficulty. The liquefied gas was first obtained by Olszewski[4] in 1886, and the pure gas itself by Stock and Doht[5] in 1901. A gas containing as much as 14 per cent. of stibine is first prepared by gradually bringing a powdered alloy of 1 part of antimony and 2 parts of magnesium, prepared by heating the constituents to redness in an atmosphere of hydrogen, into hydrochloric acid of sp. gr. 1·06 at 0°, which has been previously boiled. When this gas is washed through water, dried over calcium chloride and phosphoric oxide, and cooled by liquid air, it yields a white mass of solid stibine, and this on evaporation gives pure stibine, free from admixed hydrogen. The gas thus prepared can be collected over mercury, and when dry can be preserved for some hours without undergoing decomposition. It is a colourless gas with a characteristic odour, faintly resembling that of sulphuretted hydrogen, and is very poisonous. It condenses to a colourless liquid, which boils at $-17°$, and solidifies to a white mass, melting at $-88°$. The density of the gas is 4·36 at 15° and 760 mm., this being about 2·95 per cent. greater than the calculated normal density. The density of the liquid is 2·26 at $-25°$. Water dissolves about 0·2 vol. of the gas, and in the absence of impurities the solution is stable for some time, whilst in the presence of mere traces of air decomposition sets in rapidly. Alcohol dissolves 15 vols. of the gas, and carbon

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[1] *Phil. Mag.*, 1837, (3), **10**, 353.

[2] *Pogg. Ann.*, 1837, **42**, 339.

[3] See Jones, *Journ. Chem. Soc.*, 1876, **29**, i., 641.

[4] *Monatsh.*, 1886, 7, 371; *Ber.*, 1901, **34**, 3592.

[5] *Ber.*, 1901, **34**, 2339; 1902, **35**, 2270; Stock and Guttmann, *ibid.*, 1904, **37**, 885.

disulphide 250 vols., but both these solutions are very unstable. Stibine decomposes slowly at the ordinary temperature into antimony and hydrogen, one volume yielding 1·544 vols. of hydrogen. The rate of decomposition has been carefully studied,[1] and is greatly accelerated by the presence of water, of metallic antimony, or of hydrogen chloride. The gas is formed from its elements with absorption of 84,500 cal.,[2] and explodes when a spark is passed through it, or when it is strongly heated. Spontaneous explosion also occurs occasionally and may extend to the liquid.

Stibine is very readily decomposed by oxygen and air, with formation of water and metallic antimony, and is also attacked by nitric and nitrous oxides, and explodes when brought into contact with chlorine. It is easily inflammable, burning with a greyish flame, and evolving white fumes of antimony oxide. If passed through a glass tube heated above 150° metallic antimony is deposited close to the heated spot in the form of a lustrous mirror, and if this be heated more strongly, microscopic metallic globules are formed. Concentrated sulphuric acid decomposes the gas. Caustic alkali solution becomes deep brown when the gas is passed through it, and at last a black powder separates out. The brown solution absorbs oxygen rapidly, and especially if it be shaken with air. The powder appears to possess the composition $Sb(OH)_3$. It rapidly decomposes on standing, becoming richer in antimony. When antimony hydride is passed through a solution of silver nitrate, black silver antimonide, $SbAg_3$,[3] is first formed; the excess of silver nitrate present, however, causes a further reaction to take place, and the final precipitate consists of silver and antimony hydroxide, with a little metallic antimony.[4] Sulphur decomposes the gas, becoming covered with a film of the orange-red antimony sulphide (Jones):

$$2SbH_3 + 6S = Sb_2S_3 + 3H_2S.$$

Sulphuretted hydrogen has no action on the pure gas, but readily decomposes the impure mixture with hydrogen.

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[1] Stock and Guttmann, *Ber.*, 1904, **37**, 901, 1957; Bodenstein, *ibid.*, 1904, **37**, 1361; Stock, Gomolka, and Heynemann, *ibid.*, 1907, **40**, 532; Stock, Echeandia, and Voigt, *ibid.*, 1908, **41**, 1309.

[2] Berthelot and Petit, *Compt. rend.*, 1889, **108**, 546.

[3] Lassaigne, *J. Chim. Méd.*, 1840, **17**, 443.

[4] Reckleben, *Ber.*, 1909, **42**, 1458; see also Vitali, *L'Orosi*, 1892, 397.

ANTIMONY AND OXYGEN.

449 Considerable doubt formerly existed as to the number of the oxides formed by antimony. Thénard, in 1800, mentions several; whilst Proust, in 1804, admitted the existence of only two. The exact number was ascertained by Berzelius in 1812 to be as follows:

Antimony trioxide, Sb_4O_6,
Antimony tetroxide, Sb_2O_4,
Antimony pentoxide, Sb_2O_5.

All these are acid-forming oxides, the first acting also as a feebly basic oxide.

Antimony Trioxide, Sb_4O_6.—This occurs as the mineral valentinite with other ores of antimony, having been produced by the oxidation of these. It forms pearly-white, rhombic crystals which are sometimes coloured yellow or red by the presence of iron and other metals, and have a specific gravity of 5·566. Another, though less frequent, form of antimony trioxide is senarmontite, which usually occurs together with other antimony ores, and crystallises in regular octahedra, having a specific gravity of 5·2 to 5·3. From this it appears that antimony trioxide is isodimorphous with arsenious oxide (p. 238). Both these crystalline forms can be artificially prepared. Thus when the metal or sulphide is heated in an inclined crucible a light, white oxide is formed at a red heat, and this when more strongly heated is deposited on the upper part of the crucible in glistening needles, sometimes mixed with octahedra, and known as *flores antimonii*, or flowers of antimony. This latter form is also observed when the rhombic oxide is sublimed, and the octahedra, when quickly heated, are converted into the rhombic crystals.[1] Both forms are also obtained by crystallising a hot saturated solution of the oxide or chloride in sodium carbonate (Mitscherlich). Antimony trioxide is prepared by diluting an acid solution of the oxide with water, and washing the basic salts which are thrown down, first with hot water, then with sodium carbonate solution, again with water, and finally converting the residue into oxide by ignition. Obtained in this way, the oxide is a pale buff-coloured, crystalline powder, which can also be obtained, but not perfectly pure, by oxidising the metal with very dilute nitric acid. It is scarcely soluble in water, and becomes yellow when ignited, but assumes the pale buff tint again on cooling.

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[1] Terreil, *Compt. rend.*, 1866, 62, 302.

At a dark red heat it melts, and the mass obtained on cooling is crystalline. It volatilises at 1560°, yielding a vapour having a specific gravity of 19·9, corresponding to the molecular formula Sb_4O_6.[1] It is insoluble in dilute sulphuric acid and in nitric acid, but is easily soluble in hydrochloric and tartaric acids and the caustic alkalis. The solution of antimony trioxide in cream of tartar yields *potassium antimonyl tartrate* or *tartar emetic*, $C_4H_4KSbO_7$. Heated in the air it absorbs oxygen, the tetroxide[2] being formed at all temperatures between 390° and 775°; at very high temperatures, however, the latter decomposes and the trioxide is again formed.[3] The trioxide is readily reduced when it is heated in hydrogen. According to Bunsen, the presence of higher oxides can be easily detected by the addition of potassium iodide to the hydrochloric acid solution, when iodine is set free, as may be readily ascertained by shaking the liquid with a few drops of carbon disulphide.

The trioxide in solution is readily converted into antimonic acid by means of oxidising agents such as iodine, chlorine, or potassium dichromate, but the change cannot be completely effected by bromine water, nitric acid, or potassium chlorate and hydrochloric acid.[4] It reduces the salts of many of the metals.[5]

The mineral valentinite was probably known to the ancients. Pliny states that two kinds of stibium exist: "*Duo ejus genera mas et femina. Horridior est mas scabriorque et minus ponderosus, minusque radians et arsenosior; femina contra nitet, friabilis, fissurisque, non globis, dehiscens.*" Perhaps, however, under the feminine variety he may have understood the preparation obtained by roasting the sulphide, for this process is mentioned by Dioscorides, and Glauber also refers to it. The operation is more fully described by "Basil Valentine." He says that by regulating the fire carefully "from the common regulus of the spiessglas magnificently fine *flores* may be prepared, both yellow, red, and white," Valentine certainly knew that the mineral which we now call valentinite is an ore of antimony, for he distinguishes between the black and the golden spiessglas. The oxide obtained by roasting the metal reduced by iron was formerly called *nixferrum*, as it was believed that iron was necessary for its formation.

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[1] V. and C. Meyer, *Ber.*, 1879, **12**, 1282.

[2] Carnelley and Walker, *Journ. Chem. Soc.*, 1887, **53**, 86.

[3] Read, *ibid.*, 1894, **65**, 314; Baubigny, *Compt. rend.*, 1897, **124**, 499, 560.

[4] Bošek, *ibid.*, 1895, **68**, [1], 515.

[5] Harding, *Zeit. anorg. Chem.*, 1899, **20**, 235.

Antimony trioxide acts as a weak acid-forming oxide and also as a weak basic oxide. The salts with strong acids are decomposed by water with formation of basic salts, which in contact with water are gradually converted into the oxide.

Antimonious Acid.—Two hydrates of antimony trioxide have been described, which may be considered as the ortho- and pyro-acids, although it is not certain that they are definite compounds, since the amount of water contained in them varies gradually with the temperature at which they are dried. The ortho-acid, H_3SbO_3, is obtained by adding nitric acid to antimonyl tartaric acid or tartar emetic, and drying the precipitate at 100°. The pyro-acid, $H_4Sb_2O_5$, is formed by adding copper sulphate to a solution of antimony sulphide in caustic potash until no further orange-coloured precipitate is thrown down, but a white precipitate is formed. After filtration, the liquid, on addition of acetic acid, yields a precipitate having the above composition.[1]

Only sodium and potassium salts have as yet been obtained in the crystalline condition, and these appear to be salts of the (unknown) meta-acid, $HSbO_2$.

Sodium Antimonite, $NaSbO_2,3H_2O$, separates out from a hot solution of the oxide in caustic soda in glistening octahedra, which are sparingly soluble in water.

Hydrogen Sodium Antimonite, $NaSbO_2,2HSbO_2$, is obtained from very concentrated solutions in large crystals almost insoluble in water, which, like those of the former compound, appear to belong to the monoclinic system.[2]

Potassium Triantimonite, $K_2O,3Sb_2O_3$, is formed in crystals when the trioxide is boiled with caustic potash.[3]

Antimony Tetroxide or *Antimonious-antimonic Oxide*, Sb_2O_4.—This oxide is a white powder formed when either of the two other oxides is strongly heated in the air. When heated it becomes temporarily yellow, and dissolves only with difficulty in acids. Antimony-ash, obtained by roasting the sulphide in the air, is an impure tetroxide, and was formerly employed for the preparation of the antimony compounds. Impure tetroxide also occurs as the mineral cervantite, found together with other antimony ores in Tuscany. Antimony tetroxide forms salts with basic oxides which have been termed *hypoantimonates.*

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[1] Schaffner, *Annalen*, 1844, **51**, 182.

[2] Terreil, *Ann. Chim. Phys.*, 1866, [4], 7, 380.

[3] Cormimbœuf, *Compt. rend.*, 1892, **115**, 1305.

Potassium Hypoantimonate, $K_2Sb_4O_5$, obtained by fusing together the tetroxide and potash and lixiviating with cold water, is a white mass soluble in hot water; addition of hydrochloric acid to this solution precipitates the salt $K_2Sb_4O_9$.

Other insoluble hypoantimonates can be obtained by double decomposition with the corresponding salts. Some of these occur as minerals. Thus romeite, $CaSb_2O_5$, crystallises in tetragonal pyramids, and is found at St. Marcel, in Piedmont; and ammiolite which occurs as a powder coloured red by the presence of cinnabar, found in Chili, is probably a copper hypoantimonate, $CuSb_2O_5$.

ANTIMONY PENTOXIDE AND THE ANTIMONIC ACIDS.

450 *Antimony Pentoxide*, Sb_2O_5, is obtained by rapidly evaporating the powdered metal or its lower oxides with nitric acid and gently heating the residue. This product usually contains a small amount of the lower oxides, but the pure oxide may be prepared by gently heating the precipitate produced by adding dilute nitric acid to a solution of potassium antimonate. It is a light yellow powder, having a specific gravity of 5·6, practically insoluble in water, and turning blue litmus paper red. Nitric acid does not dissolve it, whilst concentrated hydrochloric acid dissolves it only slowly, but completely; it volatilises completely when heated with sal-ammoniac. It is reduced to the trioxide when it is heated with hydriodic acid, or treated with stannous chloride solution. Antimony pentoxide acts as a stronger acid-forming oxide than the trioxide, and at the same time as a weaker base, the only stable salts being the sulphide, fluoride, and chloride, of the typical formula SbR^I_5.

Antimonic Acid.—Antimony pentoxide is said to form several distinct hydrates, which correspond in composition to the hydrates of phosphorus pentoxide, and are known by similar names. A certain amount of confusion exists in the nomenclature of these acids since Berzelius gave the name of antimonic acid to the hydrate, $HSbO_3$, the true metantimonic acid, whereas the true pyroantimonic acid, $H_4Sb_2O_7$, was termed metantimonic acid by Frémy, and the same system extended to the salts.

The hydrated pentoxide which is formed by the action of cold water on the pentachloride, or by oxidising antimony trichloride with nitric acid, and precipitating by water, is moderately soluble in water. According to Delacroix,[1] this solution contains pyroantimonic or tetra-antimonic acid, which is converted by boiling into the ortho- or tri-antimonic acid, and yields salts of the types $M_2O,4Sb_2O_5$ and $M_2O,2Sb_2O_5$, whereas Senderens[2] describes the preparation of metantimonates from the same solution.

The *ortho-acid*, H_3SbO_4, is formed when potassium antimonate is decomposed by dilute nitric acid and the precipitate dried at 100°. The *meta-acid*, $HSbO_3$, is formed when this is heated to 175°. These substances are white powders which are soluble in aqueous potash, slightly soluble in water, and are converted into the pentoxide when heated. The meta-acid was formerly employed as a medicine under the name of *materia perlata*.

The *pyro-acid*, $H_4Sb_2O_7$ (Frémy's metantimonic acid), is formed by the decomposition of the pentachloride by hot water. The air-dried precipitate[3] possesses the formula $H_4Sb_2O_7,2H_2O$, and has the same composition as volgerite, a mineral which occurs in the province of Constantine, in Algeria.

The composition and properties of all the hydrates of antimony pentoxide which have been prepared in the solid state depend on the mode of preparation and the temperature at which they have been dried, and according to the recent investigations of Jander[4] no really definite hydrates exist.

The Antimonates.—Since the time of Berzelius, the antimonates have been chiefly investigated by Frémy,[5] Heffter,[6] Beilstein and Bläse,[7] Knorre and Olschewsky,[8] Ebel,[9] Delacroix, and Senderens. Doubt still exists as to the constitution of these compounds, since most of them contain water, which may be water of constitution or of crystallisation.

Potassium Antimonate, $KSbO_3$, is obtained by deflagrating 1 part of metallic antimony with 4 parts of saltpetre and lixiviating with warm water. A white powder is thus obtained, which when boiled for some time with water dissolves to a considerable extent. On concentrating the solution to a certain point, a crystalline mass separates, but if the liquid be further evaporated, a gum-like mass, $2KSbO_3,nH_2O$, is obtained which dissolves readily in warm water. When dried at 100° this salt contains $3H_2O$, and at 185° still contains $2H_2O$. When a current of carbon dioxide is passed through a solution of the normal salt, a sparingly soluble acid salt is precipitated which has the formula $2K_2O,3Sb_2O_5,7H_2O$ at 100°, and still contains $2H_2O$ at 350°. This salt was probably known to the iatro-chemists, and was much employed by quack doctors and known as *antimonium diaphoreticum ablutum*. The substance obtained by deflagrating the sulphide with saltpetre was employed at the end of the seventeenth century under the name *antimonium diaphoreticum non ablutum*, and Libavius and others treated this residue with acids in order to obtain their diaphoreticum, which, therefore, consisted chiefly of antimonic acid.

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[1] *J. Pharm.*, 1897, [6], **6**, 337; *Bull. Soc. chim.*, 1899, [3], **21**, 1049; 1900, [3], **25**, 288.

[2] *Bull. Soc. chim.*, 1899, [3], **21**, 47. But see also Tomula, *Zeit. anorg. Chem.*, 1921, **118**, 81.

[3] Daubrawa, *Annalen*, 1877, **186**, 110.

[4] *Kolloid Zeit.*, 1918, **23**, 122.

[5] *Ann. Chim. Phys.*, 1844, [3], **12**, 499; 1848, [3], **23**, 497.

[6] *Pogg. Ann.*, 1852, **86**, 418.

[7] *Journ. Chem. Soc.*, 1889, **56**, 1123.

[8] *Ber.*, 1887, **20**, 3043.

[9] *Ibid.*, 1889, **22**, 3044.

Normal Potassium Pyroantimonate, $K_4Sb_2O_7$, was described by Frémy (under the name of metantimonate), but the substance obtained by him was probably a mixture of caustic potash and potassium antimonate. A sparingly soluble *acid salt*, $K_2H_2Sb_2O_7,7H_2O$, can, however, be prepared by oxidising an alkaline solution of potassium antimonite with potassium permanganate and evaporating the filtrate.[1]

Sodium Antimonate, $2NaSbO_3,7H_2O$, is obtained when the metal or sulphide is deflagrated with Chili saltpetre and the mass washed out with water. At 200° it loses two molecules of water, and becomes anhydrous at a red heat.

A salt which is probably identical with this is formed as a voluminous white precipitate when sodium chloride is added to a solution of the gummy potassium antimonate. This changes on standing into the crystalline *acid sodium pyroantimonate*, $H_2Na_2Sb_2O_7,6H_2O$. It is only soluble in 350 parts of cold water, and is one of the least soluble of the inorganic salts of sodium. A solution of potassium antimonate can therefore be used as a reagent for the detection of sodium. Even when a solution contains only 0·1 per cent. of sodium salt a crystalline powder separates out after standing for twelve hours. Addition of alcohol facilitates the precipitation; free alkalis, on the other hand, retard its formation. The salts of lithium, ammonium, and the metals of the alkaline earths give precipitates with potassium metantimonate, and hence these substances must be removed from solution before the above test for sodium can be applied.

Ammonium Antimonate, NH_4SbO_3, formed by dissolving the acid in warm ammonia, separates out on cooling as a crystalline powder, insoluble in water, and readily gives off ammonia. This is the only ammonium antimonate known.[1]

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[1] Knorre and Olschewsky, *Ber.*, 1885, **18**, 2353.

Many other salts have been prepared by the action of alkalis and metallic acetates on a solution of hydrated antimonic oxide in water (Delacroix, Senderens).

The antimonates of metals of the other groups are either sparingly soluble or insoluble in water. They may be obtained by double decomposition as crystalline precipitates, which are decomposed by weak acids with formation of acid salts, whilst stronger acids, on the other hand, liberate antimonic acid. Almost all the antimonates dissolve in strong hydrochloric acid.

Normal Lead Antimonate, $Pb(SbO_3)_2$, is a white, curdy precipitate, insoluble in water. The *basic salt*, $Pb_3(SbO_3)_2(OH)_4.2H_2O$, occurs as bleinierite, at Nertschinsk, in Siberia, and Endellion, in Cornwall, in reniform or spheroidal masses, which possess a resinous appearance and a white, grey, brown, or yellowish colour. Another basic salt, used in oil painting under the name of Naples yellow, is obtained by heating a mixture of 1 part of tartar emetic, 2 parts of lead nitrate, and 4 parts of common salt for two hours to the fusing point of sodium chloride, and lixiviating with water.

ANTIMONY AND THE HALOGENS.

451 *Antimony Trifluoride*, SbF_3, is obtained as a dense snow-white mass by distilling antimony with mercury fluoride. If a solution of the oxide in an excess of hydrofluoric acid be evaporated, the fluoride is also obtained in rhombic pyramids. It is deliquescent, and is not decomposed by water; but if the solution be evaporated without an excess of hydrofluoric acid a basic fluoride is formed. Antimony trifluoride forms crystalline double salts with one, two, or three molecular proportions of the fluorides of the alkali metals. The potassium salt is used in calico printing.

Antimony Pentafluoride, SbF_5, is obtained by boiling antimony pentachloride with anhydrous hydrofluoric acid in a platinum retort provided with a reflux condenser of platinum for three days and fractionally distilling the residue.[2] It is a thick, colourless liquid of specific gravity 2·993 at 22·7°; it boils at 150°, solidifying when cooled. It attacks the skin, and dissolves paraffin, but has no action on dry glass. Exposed to air it unites with water, forming a hydrate with $2H_2O$. It combines with antimony trifluoride, with evolution of heat and contraction, forming a series of additive compounds, varying in composition from $SbF_5,2SbF_3$ to $SbF_5,5SbF_3$. The pentafluoride forms difficultly crystallisable double salts with the fluorides of the alkali metals.[1] Chlorine has no action on it, but bromine forms a viscid, dark brown mass, probably containing SbF_5Br. Iodine also reacts on the pentafluoride with development of heat and the formation of a bluish-green liquid or of a dark brown solid.

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[1] Raschig, *Ber.*, 1885, 18, 2743.

[2] Ruff and Plato, *ibid.*, 1904, 37, 673. See also *ibid.*, 1906, 39, 4310; 1909, 42, 4021.

Antimony Trichloride, $SbCl_3$.—"Basil Valentine" says: "Take of fine white, well-sublimed corrosive sublimate, and of good spiessglas the same quantity. Rub these up together and distil them. The oil which comes over is at first white, and congeals like ice or clots of butter." This preparation was termed *butyrum antimonii*, and was supposed to contain quicksilver until Glauber, in 1648, showed that this was not the case, inasmuch as it could be prepared by distilling spiessglas with oil of vitriol and common salt or hydrochloric acid. Other methods of preparation are by heating sulphate of antimony with sodium chloride, and by heating an excess of metallic antimony, or its sulphide, in a current of dry chlorine.

Antimony trichloride is a crystalline mass, melting at 73·2° and boiling at 223·5° (Kopp).[2] Its colourless vapour has the normal specific gravity of 7·8 and the salt dissolved in ether has the normal molecular weight.[3] Its latent heat of fusion is 13·37 cal. On exposure to moist air the solid deliquesces to a clear liquid, and this, on evaporation over sulphuric acid, yields crystals of the anhydrous chloride. A solution of the chloride is best obtained by boiling the sulphide with strong hydrochloric acid. When this is distilled in a retort, water comes over first, next the excess of hydrochloric acid, and lastly the anhydrous chloride. The concentrated solution, which has a specific gravity of 1·35, is known as *liquid butter of antimony*, and is employed for giving a brown surface to iron and steel wares, such, for instance, as gun-barrels (brown Bess); it is also sometimes used for pharmaceutical purposes. The anhydrous chloride yields with dry ammonia the brittle white compound $SbCl_3,NH_3$, which, on heating, gives off ammonia. It combines with hydrochloric acid to form the crystalline compound $2SbCl_3,HCl,2H_2O$, and also forms soluble crystalline double salts with a variety of metallic chlorides.[1]

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[1] Marignac, *Annalen*, 1868, **145**, 239.

[2] See also Beckmann, *Zeit. anorg. Chem.*, 1906, **51**, 96.

[3] Lespieau, *Compt. rend.*, 1897, **125**, 1094.

Powder of Algaroth.—If the acid solution of the chloride be diluted with water a white precipitate of the basic chloride is thrown down. This was known to Paracelsus, who employed it as a medicine, and states in his *Archidoxa* that in order to prepare it, corrosive sublimate is to be distilled with antimony, and the product coagulated with water, when the *mercurius vitæ* is obtained. Towards the end of the sixteenth century it was much employed, especially by the Veronese physician, Algarotus, and was termed by him *pulvis angelicus*, although it has been generally known as *powder of Algaroth*. The presence of tartaric or free hydrochloric acid prevents the precipitation of this substance. Its composition varies according to the method of its preparation. If ten parts of solid trichloride are mixed with seventeen parts of water, and allowed to stand until the precipitate has become crystalline, the compound SbOCl is deposited in small rhombohedra. These may be washed with ether in order to remove the excess of the chloride. The same compound is obtained by heating equal parts of the trichloride and absolute alcohol in sealed tubes to 140°. If one part of the trichloride be mixed with three parts of water, and the precipitate filtered off quickly and mixed with ether, the same body is obtained as an amorphous powder. When this substance is heated the trichloride is given off, and the oxychloride, $Sb_4O_5Cl_2$, remains behind. The last named compound is formed as an amorphous precipitate when the chloride is mixed with from five to fifty parts of water; on standing, it gradually forms silky prisms. If three times its bulk of hot water be added to the trichloride, and the liquid allowed to stand at 60° for some hours, crystals are obtained resembling soda crystals, which also possess the composition $Sb_4O_5Cl_2$.[2] With larger quantities of water still more basic chlorides are formed, which if boiled repeatedly with water, are converted into the trioxide, this reaction taking place more quickly in the presence of sodium carbonate. If antimony oxide be dissolved in boiling antimony trichloride, a pearl-grey, crystalline mass is obtained having the composition $SbOCl,7SbCl_3$, and this yields the substance $2SbOCl,Sb_2O_3$ on treatment with absolute alcohol.

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[1] See Ephraim, *Ber.*, 1903, 36, 1815.

[2] Sabanajew, *Zeit. Chem.*, 1871, 204.

Antimony Pentachloride, $SbCl_5$, was discovered by H. Rose in 1835, and is prepared by the direct union of antimony and chlorine, which takes place with evolution of light and heat. It is also readily formed by saturating the fused trichloride with chlorine gas. Antimony pentachloride is a yellow, fuming, disagreeably-smelling liquid, which solidifies in a freezing mixture, forming crystals melting at 3°.[1] It is readily volatile, partially decomposing on distillation into chlorine and trichloride, but under a pressure of 22 mm. it boils without decomposition at 79°, whilst under the same conditions the trichloride boils at 113·5°.[2] The vapour density[3] under a pressure of 58 mm. at 218° is 10, the calculated number being 10·3. When brought in contact with the requisite quantity of ice-cold water it forms the monohydrate,[4] $SbCl_5,H_2O$, crystallising from chloroform in thin, deliquescent scales melting at 90°. If more water be added[5] a clear liquid is obtained, and this, on standing over sulphuric acid, deposits crystals of $SbCl_5,4H_2O$, which are insoluble in chloroform (Anschütz and Evans). Hot water produces antimonic acid. As it easily loses chlorine, antimony pentachloride is employed in organic chemistry as a chlorine carrier in the chlorination of many bodies. With hydrocyanic acid it forms the white, crystalline compound $SbCl_5,3HCN$ which volatilises under 100° with partial decomposition. It also forms solid compounds with various chlorides, oxides, etc., such as $SbCl_5,SCl_4$; $SbCl_5,PCl_5$; $SbCl_5,POCl_3$; $2SbCl_5,5NOCl$; $SbCl_5,NO$; $3SbCl_5,2NO_2$; $SbCl_5,N_4S_4$. By the interaction of antimony pentachloride and iodine the addition compounds $SbCl_5,2ICl$ and $SbCl_5,3ICl$ have been obtained as bluish-black crystals melting at 62–63°.[6]

Antimony pentachloride forms a very large number of double salts, many of which are derived from the complex *metachloroantimonic acid*, $HSbCl_6$, which is obtained in greenish-yellow prisms containing $4\frac{1}{2}H_2O$ by the action of chlorine and hydrogen chloride on a solution of antimony trichloride.[7]

Antimony Tetrachloride, $SbCl_4$, is probably present in the dark brown solution formed by the action of chlorine on an excess of antimony trichloride. A number of salts have been prepared of the type $M^1_2SbCl_6$, which appear to be derived from the tetrachloride and are characterised by their dark colour. They are isomorphous with the corresponding salts of the tetrachlorides of lead, tin, and platinum.[1] The *rubidium* salt, Rb_2SbCl_6, is obtained by adding rubidium chloride to a mixture of equal molecular proportions of the tri- and penta-chlorides of antimony in presence of hydrochloric acid. It crystallises in lustrous, dark violet microscopic octahedra, and is decomposed by water. Analogous bromine compounds appear also to exist.

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[1] Moles, *Anal. Fis. Quim.*, 1914, **12**, 314.

[2] Anschütz and Evans, *Ber.*, 1886, **19**, 1994; *Journ. Chem. Soc.*, 1886, **49**, 708.

[3] Anschütz and Evans, *Annalen*, 1889, **253**, 96.

[4] *Ibid.*, 1887, **239**, 239.

[5] Weber, *Annalen*, 1863, **125**, 86.

[6] Ruff, *Ber.*, 1915, **48**, 2068.

[7] Weinland and Schmid, *Zeit. anorg. Chem.*, 1905, **44**, 37. See also *Ber.*, 1901, **34**, 2083; 1903, **36**, 244.

Antimony Tribromide, $SbBr_3$.—Powdered antimony combines directly with bromine with evolution of light and heat. The tribromide sublimes in colourless, deliquescent needles, which melt at 95° and boil at 275°; water decomposes it with formation of a basic bromide. Another method of preparation consists in heating an excess of powdered antimony with a solution of bromine in carbon disulphide; the tribromide thus obtained on evaporation crystallises in octahedra.

The *pentabromide* is obtained in combination with ether when the metal is covered with ether and treated with excess of bromine. The compound forms grey crystals and is very unstable.[2]

Antimony Tri-iodide, SbI_3.—Antimony and iodine combine directly with evolution of so much heat that if large quantities are employed explosions may ensue. The tri-iodide is a brownish-red mass, which crystallises in red, six-sided tablets from solution in carbon disulphide. It melts at 171° to a garnet-red liquid and forms a violet-red vapour, which at a higher temperature becomes scarlet. It sublimes at a temperature slightly above its melting point, boils between 414° and 427°, and is decomposed by water, with formation of a yellow oxy-iodide, which forms crystalline double salts with the various iodides.

Both the bromide and iodide form numerous double salts.

ANTIMONY AND THE SULPHUR GROUP.

452 *Antimony Trisulphide*, Sb_2S_3, occurs crystallised as stibnite in the older stratified rocks. This is the most important ore of antimony, and it is found in considerable quantity, occurring in Cornwall, Hungary, Transylvania, in the Banat, in the Harz,

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[1] Setterberg, *Ofver. K. Vetensk. akad. För.*, 1882, 23; Weinland and Feige, *Ber.*, 1903, **36**, 259; Weinland and Schmid, *ibid.*, 1905, **38**, 1080.

[2] Raynaud, *Bull. Soc. chim.*, 1920, **27**, 411.

in Westphalia, in the Black Forest, in Bohemia, in the Auvergne, in Estramadura, Algiers, Corsica, Siberia, Nevada, New Brunswick, in Japan, where it is found in magnificently large and perfect crystals, and in Borneo in large quantities. It crystallises in prisms, but is usually found in columnar or striated masses, which soil the fingers like graphite. It is easily pulverisable, and readily fusible, and has a specific gravity of 4·62. The crude sulphide occurring in commerce is obtained by melting the ore in the manner already described, and is sold in rounded masses having the form of the vessel in which the molten sulphide solidifies. It has a metallic lustre, steel-grey streak, and crystalline fracture. From early times this substance has been used in the East under the name of Kohl. The alchemists occupied themselves much with the properties of this body, as it was used for the purification of gold, and was termed *judex ultimus* or *lupus metallorum*. Antimony trisulphide also exists in the amorphous state, and in this form was known to "Basil Valentine." He states that crude spiessglas may be sublimed with formation of a red body when it is mixed with *sal ammoniacum*. In this way antimony chloride and ammonium sulphide are formed, which again react on cooling, producing the original compounds, the antimony sulphide separating out as a red powder. Glauber, and also Lemery, speak of the solution and the subsequent precipitation of the spiessglas with caustic alkalis; but it was not until 1714 that attention was directed to the red sulphide of antimony. In this year a Carthusian monk whose life had been despaired of by the Paris faculty was saved by a monk of the name of Simon administering to him a medicine which was first prepared by a German apothecary, a disciple of Glauber, and which was bought by the Parisian apothecary de la Ligére. This was soon known as the "poudre des chartreux," or Carthusian powder. Simon, however, gave to it the name of *Alkermes mineral*, and such was the reputation which this medicine enjoyed that the French Government bought the receipt for its preparation in 1720 from de la Ligérie. The process consisted in boiling the spiessglas with potashes and allowing the clear solution to cool, when the kermes was deposited as a red powder. In 1728 Stabel found that when caustic potash was employed, a red powder was also obtained, which Mender in 1738 showed to be pure kermes, and C. J. Geoffroy in 1735 proved that the same preparation was obtained when spiessglas was fused with carbonates of the alkali metals, and the liver of antimony thus obtained boiled with water. This body was believed to be a compound of antimony, sulphur, and alkali, though chemists such as Baumé denied that it contained any alkali, and assumed that in spiessglas regulus of antimony was combined with sulphur, whilst in mineral kermes calx of antimony was combined with sulphur. Many other views were held concerning the composition of this compound until Rose in 1825, and Fuchs in 1833, showed that mineral kermes is merely amorphous antimony sulphide.

Various methods may be adopted for the preparation of mineral kermes, which for fifty years was highly prized as a medicine, and even now is sometimes employed. All these processes yield a preparation containing, as impurity, varying quantities of antimony oxide, both free and combined with the alkalis, and moreover on exposure to air oxidation occurs with formation of the oxide and free sulphur.[1] Hence the preparation of the kermes should be carried on exactly according to the prescription of the pharmacopœia.

In order to prepare the amorphous sulphide free from oxide, the crystalline compound is boiled with caustic potash in absence of air, the liquid filtered, and the hot diluted solution precipitated with sulphuric acid. The precipitate is then washed with very dilute acid, and afterwards with cold water; and to remove any oxide which may be present it is heated with a solution of tartaric acid. Thus obtained, the precipitate becomes anhydrous when dried at 100° and forms a reddish-brown, light powder which readily soils the fingers. This is more soluble in hydrochloric acid, in the fixed alkalis and their carbonates than the crystalline compound into which it is converted on fusion. It may also be obtained by pouring fused stibnite into an excess of cold water. It then forms an amorphous, lead-grey mass which appears of a hyacinth-red colour when seen in thin films, has a specific gravity of 4·15, and when triturated is converted into a dark reddish-brown powder.

If sulphuretted hydrogen is passed into an acid solution of the trichloride or into an acidified solution of tartar emetic, an orange-red precipitate of amorphous hydrated sulphide is obtained, which after drying at 100—130° becomes black at 200°. The precipitated sulphide also becomes black when it is boiled with 2 parts of hydrochloric acid and 1 part of water in a current of carbon dioxide.[2]

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[1] Pollacci, *Boll. Chim. farm.*, 1906, 45, 401.

[2] Mitchell, *Chem. News*, 1893, 67, 291. See also de Bacho, *Ann. chim. applicata*, 1919, 12, 143; Wilson and McCrosky, *J. Amer. Chem. Soc.*, 1921, 43, 2178.

When the sulphide is heated at 850° in nitrogen, and the vapours are rapidly condensed, black needles are formed accompanied by lilac-coloured globules which appear to constitute a polymorphic variety of the sulphide.[1] This form has the specific gravity 4·278 at 0°, and passes at 220° into the black, crystalline form, of specific gravity 4·652 and melting[2] at 540°.

When a dilute solution of tartar emetic is added to sulphuretted hydrogen water a colloidal solution of antimony sulphide is produced, which is orange-red by transmitted light, and can be boiled without undergoing change. Calcium chloride and many other electrolytes cause an immediate precipitation of the sulphide.[3] On heating in a current of hydrogen the trisulphide is reduced to metal, but it may be sublimed without decomposition in an atmosphere of nitrogen. The equilibrium between the sulphide and hydrogen at various temperatures has been examined by Pélabon.[4] Crystalline antimony sulphide is used for the preparation of other antimony compounds, in pyrotechny, in the heads of lucifer matches, and in the composition used for firing breechloading firearms. The amorphous sulphide is largely used for vulcanising caoutchouc, to which it imparts a reddish-brown colour.

The compound known as *antimony cinnabar*, which is obtained by warming a solution of the trichloride with sodium thiosulphate, is the trisulphide. This substance is used in oil painting as well as in water-colour painting and as a distemper.

The Thioantimonites or *Livers of Antimony* are formed by the combination of the trisulphide with metallic sulphides.[5] Those of the alkali metals are prepared by fusing the constituents together. They are brown or black, and when they contain a large quantity of metallic sulphide they are easily soluble in water, but when the quantity of antimony increases, these livers of antimony become more sparingly soluble, and at last insoluble in water. They are also formed when the trisulphide is dissolved in a solution of a sulphide, or, mixed with antimonite, when the trisulphide is fused with an alkali or alkali carbonate or treated with the solution of an alkali:

$$2Sb_2S_3 + 4KOH = 3KSbS_2 + KSbO_2 + 2H_2O.$$

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[1] Guinchant and Chrétien, *Compt. rend.*, 1904, **138**, 1269; **139**, 51.

[2] See also Pélabon, *ibid.*, 1904, **138**, 277; and Zani, *Bull. Acad. roy. Belg.*, 1909, 1160.

[3] Picton, *Journ. Chem. Soc.*, 1892, **61**, 142; Biltz and Geibel, *Nachr. K. Ges. Wiss. Göttingen*, 1906, 141.

[4] *Compt. rend.*, 1900, **130**, 911.

[5] See Pouget, *ibid.*, 1897, **124**, 1445, 1518.

Acids precipitate the amorphous trisulphide from these solutions, which also absorb oxygen rapidly from the air. Many of the thioantimonites occur as minerals, and the composition of some of these has been already given.[1] The alkali salts[2] belong to the types $MSbS_2$, M_3SbS_3, $M_2Sb_4S_7$, and $M_4Sb_2S_5$.

Antimony Tetrasulphide, Sb_2S_4, and *Pentasulphide*, Sb_2S_5, do not occur in the native state. "Basil Valentine" mentions that when spiessglas is boiled with strong caustic ley, and acetic acid added to the liquor, a red body is precipitated, and Quercetanus in 1603 mentions in his pharmacopœia a preparation from spiessglas and liver of sulphur by means of acids, terming it *sulphur antimonii auratum*. In 1654 Glauber mentions in the "pharmacopœia spagyrica" the preparation obtained by precipitating the slag formed in the preparation of regulus of antimony by means of acetic acid, and recommends this product as *panacea antimonialis* or *sulphur purgans universale.* This preparation, which, as golden sulphuret of antimony, soon became a favourite medicine, was obtained from the more or less oxidised solution of liver of antimony, containing a thioantimonate. When fractionally precipitated by hydrochloric acid a brown kermes is first thrown down and afterwards a golden-coloured sulphide, termed *sulphur auratum tertiæ præcipitationis.* Later, stibnite was boiled with alkali and sulphur and the solution precipitated with acid. At the present day pure sodium thioantimonate is first prepared; this is dissolved in from 10 to 60 parts of water and a cold mixture of 3·3 parts of sulphuric acid and 100 parts of water is gradually added; the precipitate is well washed with distilled water and dried at a moderate temperature in the dark.

The *sulphur auratum* thus prepared has generally been regarded as antimony pentasulphide mixed with trisulphide and free sulphur. According to F. Kirchhoff,[3] however, it contains the tetrasulphide, Sb_2S_4, and no pentasulphide. The tetrasulphide may be obtained in the pure state by decomposing zinc thioantimonate with dilute acids, and extracting free sulphur from the precipitate by means of carbon disulphide or acetone. The zinc salt is readily obtained from Schlippe's salt by double decomposition with zinc chloride, when it forms a chrome-yellow precipitate which becomes bright orange-red when dried and powdered, and contains about 6·7 per cent. of free sulphur.

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[1] See also Sommerlad, *Zeit. anorg. Chem.*, 1897, **15**, 173; Pouget, *Compt. rend.*, 1897, **124**, 1518; 1903, **136**, 1450.

[2] See Pouget, *Compt. rend.*, 1897, **124**, 1446; 1898, **126**, 1144, 1792; Staněk, *Zeit. anorg. Chem.*, 1898, **17**, 117.

[3] *Zeit. anorg. Chem.*, 1920, **112**, 67; **114**, 266.

The pure pentasulphide is precipitated when an excess of sulphuretted hydrogen water is added to a solution containing the antimony in the form of antimonic acid at the ordinary temperature (Bunsen).[1] When sulphuretted hydrogen is passed into the antimony solution a mixture of pentasulphide, trisulphide, and sulphur is formed, the proportion of the pentasulphide diminishing as the rate at which the gas is passed is lessened and as the temperature is raised. Hydrochloric acid up to about 20 per cent. favours the production of the pentasulphide, but in larger amount hinders it.[2]

Antimony pentasulphide is a fine yellowish-red powder easily soluble in aqueous alkalis and their sulphides, and also, in absence of air, in warm ammonia. It likewise dissolves in the carbonates of the alkali metals, but not in ammonium carbonate. When exposed to sunlight, heated in water to 98°, or simply heated in absence of air, it decomposes into the black trisulphide and sulphur, and is decomposed by hot hydrochloric acid.

Sodium Thioantimonate, $Na_3SbS_4,9H_2O$.—This is termed, from the discoverer, *Schlippe's salt*, and is obtained by dissolving the trisulphide, sulphur, and caustic soda or a mixture of soda-ash and lime, in the requisite quantity of water; or by fusing together 16 parts of anhydrous sodium sulphate, 13 parts of stibnite, and 5 parts of carbon, dissolving, and boiling the solution with 2·5 parts of sulphur. It crystallises in large, colourless or yellow, regular tetrahedra which have an alkaline reaction and a saline, cooling, metallic taste resembling that of liver of sulphur. It dissolves at 15° in 2·9 parts of water and is precipitated from aqueous solution by alcohol. The hydrated crystals on exposure to moist air soon become covered with a kermes-coloured coating, and when they are heated in absence of air water is given off and the anhydrous salt formed, which fuses at a dark red heat.

Potassium Thioantimonate, $K_3SbS_4,9H_2O$, is prepared in a similar way to the sodium salt and forms deliquescent crystals.

Ammonium Thioantimonate, $(NH_4)_3SbS_4$, formed when the trisulphide and sulphur are dissolved in red ammonium sulphide, crystallises in unstable pale yellow prisms.[3]

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[1] *Annalen*, 1878, **192**, 305.

[2] Bosek, *Journ. Chem. Soc.*, 1895, **67**, 515; Brauner, *ibid.*, 527. See also Klenker, *J. pr. Chem.*, 1899, [2], **59**, 150, 353.

[3] Staněk, *Zeit. anorg. Chem.*, 1898, **17**, 117.

Barium Thioantimonate, $Ba_3(SbS_4)_2,6H_2O$, is prepared by dissolving the freshly precipitated golden sulphide of antimony in barium monosulphide and precipitating by alcohol. In this way stellate groups of needles are obtained.

The *calcium* salt is prepared in a similar way and is thrown down as an oily liquid on addition of alcohol. The thioantimonates of the alkali metals have been examined by Donk.[1] The thioantimonates of the other metals are yellow, red, brown, or black precipitates, almost entirely insoluble in water and are obtained by double decomposition.

Antimony Oxysulphide, Sb_2S_2O, is found, together with stibnite, as kermesite or antimony blende in needle-shaped crystals or thin, six-sided prisms which have a cherry-red colour and an almost metallic lustre. It is obtained as a reddish-brown powder by adding antimony trisulphide to fused antimony iodide, and treating the mass with dilute hydrochloric acid, when a dark reddish-brown, lustrous powder of antimony thio-iodide, SbSI, remains behind. When boiled with water and oxide of zinc, this is converted into the oxysulphide.

Glass of Antimony or *Vitrum Antimonii* is obtained by fusing oxidised stibnite with a small quantity of the sulphide. It forms a transparent, dark ruby-red mass, formerly largely employed for obtaining the other antimony compounds, but now used only for imparting a yellow tint to glass and porcelain.

Antimonial Saffron or *Crocus Antimonii*.—If stibnite is deflagrated with a quantity of saltpetre insufficient for complete oxidation a brownish-yellow powder is obtained on lixiviation which when heated melts to a yellow glass.

Chlorosulphides of Antimony.—Two compounds of this class, SbS_2Cl and Sb_2S_5Cl, have been obtained as reddish-brown, crystalline substances by the action of sulphuretted hydrogen on antimony trichloride at its melting point.[2] The compound $SbSCl,7SbCl_3$ is obtained by heating the trichloride and trisulphide together. Alcohol converts it into $2SbSCl,3Sb_2S_3$.

Iodosulphides of Antimony.—Compounds of the formulæ SbS_2I and SbS_2I_3 are formed when antimony trisulphide is heated with iodine (Ouvrard).

Antimony Trisulphate, $Sb_2(SO_4)_3$, is obtained as a white mass by heating either the metal or the oxide with concentrated sulphuric acid. The composition of the salt depends on the concentration of the acid used, acid or basic salts being obtained when the acid employed is stronger or weaker than that represented by the formula H_2SO_4.[1] The normal salt crystallises from a tolerably acid concentrated solution in long, glistening, silky needles,[2] and is decomposed by water into a soluble acid salt, and an insoluble basic salt. If antimony chloride be heated with fuming sulphuric acid a basic salt, $Sb_2O(SO_4)_2$, is produced in small, glistening crystals, which in contact with alcohol are transformed into the salt $Sb_2O_2SO_4$, consisting of a white powder, which, when treated with boiling water, yields the salt $Sb_4O_5SO_4$. Several other salts have also been described.

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[1] *Chem. Weekblad*, 1908, **5**, 529, 629.

[2] Ouvrard, *Compt. rend.*, 1893, **116**, 1516; **117**, 107.

Antimony sulphate yields double salts with the alkali sulphates, such as $KSb(SO_4)_2$, which crystallises in nacreous leaflets. These are decomposed by water, yielding antimonious hydroxide.[3]

Antimony Thiosulphate.—A number of complex antimony thiosulphates have been prepared by Szilágyi.[4]

453 *Antimony Triselenide*, Sb_2Se_3, is formed when the two elements are fused together, a metallic, lead-grey, crystalline mass being produced[5] which melts at 572°. When selenium hydride is passed into a solution of tartar emetic the same compound is precipitated as a black powder.

Antimony Pentaselenide, Sb_2Se_5, is precipitated as a brown powder by adding dilute sulphuric acid to a solution of sodium seleno-antimonate.

Sodium Seleno-antimonate, $Na_3SbSe_4,9H_2O$, is isomorphous with the corresponding thio-antimonate, and is obtained by fusing together sodium carbonate, antimony triselenide, selenium, and charcoal. The fused mass is boiled out with water in absence of air and the filtrate covered with a layer of strong alcohol. The salt separates out after some time in orange-red, transparent tetrahedra which are soluble in two parts of cold water and become red in air, with separation of selenium. When a solution of Schlippe's salt is boiled with selenium, filtered, and the solution concentrated in absence of air yellow tetrahedra of $Na_3SbSeS_3,9H_2O$ are deposited.

Antimony and tellurium[6] when fused together yield only one definite compound, *antimony tritelluride*, Sb_2Te_3.

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[1] Adie, *Chem. News*, 1890, **61**, 58.

[2] Schultz-Sellack, *Ber.*, 1871, **4**, 13.

[3] Gutmann, *Arch. Pharm.*, 1898, **236**, 477; Metzl, *Zeit. anorg. Chem.*, 1906, **48**, 140; German Patent 161776. See also Kühl, *Zeit. anorg. Chem.*, 1907, **54**, 256; Gutmann, *Arch. Pharm.*, 1908, **246**, 167.

[4] *Zeit. anorg. Chem.*, 1920, **113**, 69.

[5] See Pélabon, *Compt. rend.*, 1906, **142**, 207; Chrétien, *ibid.*, 1339, 1412; Chikashige and Fujita, *Mem. Coll. Sci. Kyoto*, 1917, **2**, 233.

[6] See Fay and Ashley, *Amer. Chem. J.*, 1902, **27**, 95.

ANTIMONY AND THE NITROGEN GROUP.

454 No definite nitrate of antimony is known, although the white powder obtained by the action of nitric acid on antimony contains nitrogen, and is converted by water into antimony pentoxide and nitric acid.

If phosphorus be added to fused antimony a tin-white *phosphide of antimony* is obtained which when heated in the air burns with a greyish flame.

Antimony Thiophosphate, $SbPS_4$ or Sb_2S_3,P_2S_5, is formed when the trichloride or trisulphide is heated with phosphorus pentasulphide. It is a fusible, insoluble, yellow, crystalline mass.[1]

Antimony combines directly with arsenic. The compound $SbAs_3$ occurs as allemontite in reniform or amorphous masses having a metallic lustre.

MEDICINAL USES OF ANTIMONY.

455 As we have seen, various antimony preparations are used as important medicines. Paracelsus was one of the first to employ these for internal use, and his example was followed by the other iatro-chemists, many of whom worked diligently on antimony and its compounds. The disciples of the old Galenic school were violently opposed to the introduction of the antimony compounds into medicine, and they succeeded in inducing the Paris Parliament in 1566 to prohibit the use of antimony and its compounds by all physicians on pain of having their licences withdrawn. In 1603 the medical faculty of Paris took a similar step, and this decree was not withdrawn until the year 1666.

Metallic antimony itself was at one time employed for the preparation of goblets in which wine was allowed to stand overnight in order that it might be used as an emetic; but this practice fell into disuse even during Boyle's time. Pills made of metallic antimony were employed at a later period; these were termed everlasting pills, because they, like the goblets, were believed only to act by contact and not to lose their weight. This error was first combated by Lemery and Vigani, a Veronese quack doctor who lived in England, and they showed that both antimony and fused stibnite became acted upon when placed in contact with wine.

Whilst formerly a large number of antimony compounds were employed in medicine, the only ones which are used at the present day are tartar emetic or potassium antimonyl tartrate, $C_4H_4K(SbO)O_6$, and the trisulphide or *antimonium sulphuratum*. The first compound is given in doses of 0·0027 to 0·008 gram as a diaphoretic, and from 0·065 to 0·13 gram as an emetic. The dose of the second is from 0·065 to 0·13 gram.

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[1] Glatzel, *Ber.*, 1891, **24**, 3886.

In larger doses it produces, like white arsenic, violent irritation in the intestines, vomiting and purging. When one large dose only is administered the case proceeds rapidly to recovery or death, generally the former, if the case be placed early under proper treatment, and in this respect acute antimonial is distinguished from acute arsenical poisoning.

In cases of chronic antimony poisoning the principal symptoms are dryness of the throat, pain on swallowing, nausea and vomiting, diarrhœa, loss of flesh, giddiness, fainting, and albuminuria. Death takes place from exhaustion and wasting. Several cases have occurred in this country to show that tartar emetic has been thus criminally and fatally used (Taylor).

DETECTION AND ESTIMATION OF ANTIMONY.

456 When a small quantity of an antimony compound is heated in the upper reduction zone of a Bunsen burner on a thread of asbestos the flame becomes of a bluish tinge, and when a small porcelain basin filled with cold water is held above it a brownish-black deposit of metallic antimony is found upon the basin, and this is but slightly attacked by cold nitric acid, and is insoluble in sodium hypochlorite. Arsenic gives a very similar reaction, but this may be distinguished from antimony by the fact that during the reduction a garlic-like smell of arsenic is noticed, and that the metallic film is readily soluble in sodium hypochlorite. If an antimony compound is heated on a carbonised match a brittle metallic bead is obtained, whilst arsenic is completely volatilised. Most of the antimony compounds are insoluble in water but dissolve in hydrochloric acid. Those which do not thus dissolve may be obtained in solution by fusion with potassium carbonate and saltpetre, and subsequent solution in hydrochloric acid. Sulphuretted hydrogen produces in acid solutions a very characteristic orange-red coloured precipitate of antimony trisulphide. If other metals precipitable by sulphuretted hydrogen are present, the mixed sulphides, after washing, are treated with ammonium sulphide, filtered, and the filtrate acidified with hydrochloric acid. This

precipitate may contain, together with antimony, the sulphides of tin and arsenic. This last metal is removed by digesting with freshly prepared solution of ammonium carbonate, and washing the residue with water. This is then brought into solution by heating with hydrochloric acid, and the liquid is placed in a platinum dish containing a piece of zinc; the antimony is deposited upon the platinum as a black, adherent coating, which is readily soluble in nitric acid and can then be identified as antimony. A more satisfactory method consists in dissolving the mixed sulphides in caustic soda and a few drops of yellow ammonium sulphide and then boiling with sodium peroxide, which converts the metals into stannate, antimonate, and arsenate respectively. Tin is then detected by boiling with ammonium chloride, which precipitates stannic hydroxide, and arsenic and antimony are detected in the acidified filtrate by Bunsen's method described below.[1] A rapid method of detection is to boil the sulphides with a 5 per cent. solution of sodium carbonate, which leaves tin sulphide undissolved; the solution deposits antimony sulphide on cooling, whilst arsenic sulphide remains dissolved and can be detected as usual.[2]

Antimony may also be detected by means of Marsh's test carried out as described under arsenic (Vol. I., p. 717). The mirror obtained is deposited much closer to the flame than that of arsenic, is formed at a lower temperature, does not yield a crystalline deposit of oxide when heated in the air, and is not soluble in sodium hypochlorite. When the gas is passed into silver nitrate solution, silver antimonide is precipitated (p. 1007).

Antimony trichloride gives a spark spectrum containing, among others, the following lines, mentioned in order of their relative brightness (Lecoq de Boisbaudran): α 6005, β 5568, γ 6130, δ 6079.

Antimony is usually estimated gravimetrically either as the sulphide or the tetroxide. In the first case it is obtained as a hydrated precipitate, which may also contain sulphur and pentasulphide. It is necessary therefore, to dry this at 100°, to weigh it, and to bring a known fraction into a porcelain boat contained in a glass tube. Through the tube dry carbon dioxide is passed, and the sulphide is heated, the pure anhydrous trisulphide remaining behind. The sulphide may also be oxidised by means of nitric acid and the residue ignited and weighed as tetroxide, or it may be dissolved in a large excess of sodium sulphide, potassium cyanide added, and the resulting solution electrolysed and the metal weighed.[1] Antimony is also frequently estimated volumetrically, the trioxide, in presence of sodium bicarbonate, being converted by means of standard iodine solution into the pentoxide, or the trichloride being converted into the pentachloride by a standard solution of sodium bromate in presence of hydrochloric acid.[2]

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[1] Walker, *Journ. Chem. Soc.*, 1903, 83, 184.

[2] Materne, *Bull. Soc. chim. Belg.*, 1906, 20, 46.

The *quantitative* separation[3] of antimony from other metals, with the exception of arsenic and tin, does not exhibit any difficulty. Should these three elements be present together their sulphides must be first converted into oxides by treatment with nitric acid, and these fused for some time with eight times their weight of caustic soda. The cooled mass is next allowed to soften in hot water until the sodium metantimonate has separated out as a white powder, and then one volume of alcohol of specific gravity 0·83 is added for every three volumes of the liquid. After standing for some time the liquid is filtered and the precipitate well washed with dilute alcohol, to which at last some caustic soda is added. The filtrate contains the stannate and arsenate, whilst the whole of the antimony is contained in the residue, and this is converted in the usual way into the sulphide (H. Rose). A more rapid method of separation depends on the fact that in presence of free oxalic acid antimony is precipitated by sulphuretted hydrogen as the sulphide, whereas tin remains in solution.[4] Antimony and tin can also be separated electrolytically.[5]

The separation of antimony from arsenic, which had previously been difficult and unsatisfactory, was first rendered exact by Bunsen. The moist and well-washed mixture of sulphides obtained by precipitation with sulphuretted hydrogen is dissolved on the filter in an excess of caustic potash, and the diluted solution treated with chlorine until all the free alkali has combined. The excess of chlorine is then got rid of by repeated evaporation with hydrochloric acid, the solution diluted, and this treated with a freshly prepared solution of sulphuretted hydrogen until all the antimony is precipitated. A rapid current of air is then passed through the liquid in order to expel the excess of sulphuretted hydrogen, and the precipitate washed first with water, then with alcohol, and at last repeatedly with carbon disulphide, in order to remove free sulphur. After drying at 110°, pure pentasulphide of antimony remains, and this is afterwards weighed. The arsenic in the filtrate may be estimated by continued treatment with sulphuretted hydrogen when the pentasulphide is precipitated and treated as above described.

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[1] Kohn and Barnes, *British Assoc. Reports*, 1896, 244. See also Law and Perkin, *Trans. Faraday Soc.*, 1905, **1**, 262; Hahn and Philippi, *Zeit. anorg. Chem.*, 1921, **116**, 201.

[2] Nissenson and Siedler, *Chem. Zeit.*, 1903, **27**, 740; Rowell, *J. Soc. Chem. Ind.*, 1906, **25**, 1181.

[3] See Darling, *Chem. Zentr.*, 1919, ii., 890; 1920, ii., 750 *for a bibliography of the subject.*

[4] Clarke, *Chem. News*, 1870, **21**, 124; Lesser, *Zeit. anal. Chem.*, 1888, **27**, 218; Warren, *Chem. News*, 1890, **62**, 216; Clark, *Journ. Chem. Soc.*, 1892, **61**, 424; Henz, *Zeit. anorg. Chem.*, 1903, **37**, 1.

[5] See Fischer, *Zeit. anorg. Chem.*, 1904, **42**, 363, where the literature of the subject is quoted. Compare Cohen and Morgan, *Analyst*, 1909, **34**, 3.

A still simpler method of effecting this separation consists in adding ferrous sulphate or chloride to a solution of the chlorides of the two metals in hydrochloric acid, saturating with hydrochloric acid gas, and distilling. The whole of the arsenic passes over and may be collected in dilute hydrochloric acid, whilst the antimony remains behind and may be precipitated in the usual way after the ferric salt has been reduced to the ferrous state.[1]

Atomic Weight.—The methods which have at various times been employed for the determination of the atomic weight of antimony have led to somewhat divergent results. The number 129 obtained by Berzelius was long accepted as correct, until Schneider's experiments [2] on the reduction of the sulphide proved that 120·55 was nearer the truth. Dexter [3] then found the number 122·5 by treatment of the metal and trioxide with nitric acid, the resulting oxide being converted into the tetroxide by ignition. This was confirmed by Kessler,[4] who adopted a similar plan, and by Dumas,[5] who analysed the trichloride and obtained the number 121·8. On the other hand, a very carefully conducted series of analyses of the bromide led Cooke [6] to the number 119·86, while analysis of the iodide gave 119·8 and synthesis of the sulphide 120·55. The electrolysis of the chloride led in the hands of Pfeiffer [7] and of Popper [8] to the number 121·2, but it has been shown that the method applied is not accurate.[1] A series of determinations made by Friend and Smith,[2] by the indirect method of heating potassium antimonyl tartrate in hydrogen chloride and weighing the potassium chloride produced, gave the number 120·34.

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[1] Fischer, *Ber.*, 1880, **13**, 1779. See also Piloty and Stock, *Ber.*, 1897, **30**, 1649; Beck and Fisher, *Chem. News*, 1899, **80**, 259, where a critical discussion of the various methods is to be found.

[2] *Pogg. Ann.*, 1856, **98**, 293.

[3] *Ibid.*, 1857, **100**, 563.

[4] *Ibid.*, 1861, **113**, 145.

[5] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.

[6] *Amer. J. Sci.*, 1878, **15**, 41, 107; 1880, **19**, 382.

[7] *Annalen*, 1881, **209**, 173.

[8] *Ibid.*, 1886, **233**, 153.

The value at present (1922) adopted is 120·2, which is based largely upon the work of Cooke. Nevertheless, it is quite possible that the older determinations, giving a value round about 122, are more nearly correct. A number of chemists have suggested that the higher value is preferable, basing their views upon the results of careful analytical investigations;[3] and, in an elaborate investigation into the preparation and analysis of pure antimony tribromide, Willard and McAlpine have[4] recently obtained the value 121·77.

BISMUTH. Bi = 208·0. At. No. 83.

457 The word *marcasite*, by which, up to recent times, the metal bismuth was often designated, is found in the authors of the thirteenth century. Hence it has been supposed that this metal was known at that time. This is, however, not the case, for the name marcasite had in those days, and even at a much later period, a very indefinite meaning, being given to any ore which had a metallic appearance, and especially to those ores which are now classed as pyrites.

Bismuth was classed by Paracelsus amongst the semi-metals. On the other hand, Agricola mentions *bisemutum* or *plumbum cinereum* as a true metal which is usually added to tin in order to make it work better. Notwithstanding this clear statement, it was subsequently confounded by Libavius with antimony, and by Lemery with zinc. Metallic bismuth was moreover described by "Basil Valentine" in his Last Testament: "Antimonium must be placed between tin and lead, as bismuth or magnesia is placed under and between tin and iron," and he also states that "bismuth or marcasite is a bastard *jovis*." Pott, in 1739, was the first to make us acquainted with the special properties of bismuth, and its reactions were exactly studied by Bergman.

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[1] Cohen and Strengers, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, **5**, 543.

[2] *J. Amer. Chem. Soc.*, 1901, **23**, 502.

[3] Youtz, *Zeit. anorg. Chem.*, 1903, **37**, 337; Beckett, *Inaugural Dissertation* (Zurich, 1909); von Bacho, *Monatsh.*, 1916, **37**, 100.

[4] *J. Amer. Chem. Soc.*, 1921, **43**, 797.

Bismuth is a comparatively rare metal. It is found chiefly in the native condition, but also as the oxide or bismuth ochre, Bi_2O_3; less frequently it occurs as bismuthite, Bi_2S_3, whilst it is found still more sparingly in the following minerals: telluric bismuth or tetradymite, $Bi_2(Te,S)_3$; emplectite, $Cu_2Bi_2S_4$; bismuthite, $3(BiO)_2CO_3,2Bi(OH)_3,3H_2O$; aikinite, $Bi_2S_3,2PbS,Cu_2S$; bismuthosmaltite, $Co(As,Bi)_2$; pucherite, $BiVO_4$; eulytite or bismuth silicate, $Bi_4(SiO_4)_3$, etc., and occurs in traces in the pyrites of Agordo. Native bismuth is sometimes found nearly pure, but is usually alloyed with other metals or mixed with a variety of ores. It is found in veins traversing gneiss or clayey slate in Bolivia, Saxony, Australia, etc., usually associated with ores of silver and cobalt.

468 *The Metallurgy of Bismuth.*—Formerly bismuth was obtained by heating the ore in sloping iron tubes, when merely that portion of the metal present in the elementary state was obtained, and this in a very incomplete manner. The residue was employed in the manufacture of smalt, and the bismuth again extracted from the cobalt speiss.

This liquation process has now been superseded by smelting methods. Oxidised ores may be treated direct, but sulphides must be subjected to a preliminary roast. Reduction is carried out in crucible furnaces or in small reverberatory furnaces, the charge being made up of ore, carbon, slag, sodium carbonate, limestone, and sometimes fluorspar. It is essential to have an easily fusible slag so as to avoid loss by volatilisation. The products of this operation are generally crude bismuth, matte or speiss, and slag. For ores carrying sulphide of antimony and arsenic scrap iron is also added to the charge.

Bismuthiferous litharge and other metallurgical by-products are sometimes treated with hydrochloric acid, and the bismuth precipitated by means of iron, or the solution is largely diluted with water in order to precipitate the oxychloride, which is dried and reduced.

Crude bismuth, which generally contains lead, antimony, and arsenic, besides traces of iron, cobalt, nickel, silver, and sulphur, is refined by melting it in small iron kettles under a cover of salt, potassium chloride, caustic soda, and sufficient oxychloride of bismuth to take up the lead. The mass is constantly stirred, and in from one to three hours the whole of the lead is converted into chloride, and a corresponding amount of bismuth separated from the oxychloride. Antimony is removed in the same way with a flux of soda, potash, and sulphur, sodium thioantimonate being formed, whilst for arsenic the flux used is caustic soda and nitre.[1] A simple liquation process is also often used, the metal being melted on a slightly inclined iron plate.

Bismuth which contains 1 or more per cent. of lead melts at a lower temperature than pure bismuth. Such an impure metal exhibits on cooling the peculiarity that the solid crust of pure crystallised bismuth is seen to be broken through by drops of a liquid alloy, and this property has been employed to separate bismuth from lead (Matthey). Silver behaves in a similar manner. Commercial bismuth frequently contains small quantities of gold, which, along with silver, may be removed by melting with 2 per cent. of zinc and skimming off the surface layer, which is found to contain the precious metals.[2]

When bismuth is required for pharmaceutical purposes it must be freed from traces of arsenic. For this purpose it is melted with nitre or other oxidising agent, fused with metallic iron, or the molten metal is well stirred and exposed to the air, any antimony being simultaneously oxidised.[3]

In order to prepare chemically pure bismuth, the commercially pure metal is dissolved in nitric acid and evaporated with hydrochloric acid. The chloride is then dissolved in hydrochloric acid and the solution mixed with alcohol, which precipitates the greater portion of the lead in the form of chloride. The filtrate is poured into water and the precipitated oxychloride washed, redissolved in hydrochloric acid, and again precipitated with water, this process being frequently repeated. The oxychloride is then again dissolved in hydrochloric acid and precipitated with ammonia and ammonium carbonate, this operation being repeated three times, after which it is finally reconverted into oxychloride, and the latter reduced to metal by fusion with potassium cyanide. The metal thus obtained still contains lead, from which it can only be freed by electrolysis. For this purpose it is dissolved in nitric acid and the solution slowly electrolysed, any lead being deposited as peroxide on the positive pole. The bismuth is then finally fused with potassium cyanide.[4] Another method is as follows. The fairly pure nitrate is dissolved in half its weight of 8 per cent. nitric acid, mixed with an equal weight of the concentrated acid, and cooled to 0° to −10°. The pure nitrate which crystallises out is washed with a little ice-cold nitric acid, heated to convert it into oxide, and the oxide reduced by fusion with potassium cyanide. If necessary, further purification may be carried out by melting the metal under paraffin, allowing it to crystallise in part, and removing the first and purest crystals by means of a glass spoon.[1]

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[1] Borchers, *Mineral Industry*, 1890, **8**, 62.

[2] Matthey, *Proc. Roy. Soc.*, 1887, **42**, 69.

[3] *Ibid.*, 1893, **52**, 46.

[4] Classen, *Ber.*, 1890, **23**, 940.

459 *Properties.*—Bismuth is a hard, brittle metal, having a bright, metallic lustre and a greyish-white colour, with a distinctly reddish tinge. Its specific gravity at 15° is 9·747; it melts at 271° and expands in the act of solidification, the specific gravity of the solid at the temperature of the melting point being 9·673 and that of the liquid 10·004.[2] Its boiling point lies in the neighbourhood of 1420° (Greenwood), and it can be distilled in a current of hydrogen. The vapour density between 1600° and 1700° is about 11, a number which is intermediate between the values corresponding to the formulæ Bi and Bi_2.[3] When a large quantity is melted, allowed to cool slowly until the surface begins to solidify, the crust then broken, and the liquid metal poured out, fine large crystals are obtained. These are obtuse rhombohedra which have the appearance of cubes as their angles approach closely to 90°. Acicular needles consisting of elongated, hexagonal prisms have also been observed.[4] The crystals oxidise in the air, and frequently become covered with an iridescent film of oxide. The same colours may be obtained when the metal is melted in the air, but if the heat be continued, the metal gradually becomes altogether converted into oxide; at a red heat steam is slowly decomposed by bismuth. This metal combines also directly with the elements of the chlorine group and with sulphur; hydrochloric and sulphuric acids do not act upon it in the cold, but the latter acid dissolves it on heating with evolution of sulphur dioxide. Hydrochloric acid dissolves it in the presence of dissolved oxygen. The best solvents for bismuth are nitric acid and aqua regia, both of which dissolve the metal readily in the cold.

According to Cohen, bismuth is a mixture of two or more allotropes.[5]

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[1] Mylius and Groschuff, *Zeit. anorg. Chem.*, 1910, **66**, 237.

[2] Vicentini, *Journ. Chem. Soc.*, 1891, **60**, 518.

[3] Meyer, *Ber.*, 1889, **22**, 720.

[4] Heberdey, *Sitzungsber. K. Akad. Wien*, 1895, **104**, i. 254.

[5] Cohen, *Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1236; Wurmschmidt, *Jahrb. Min.*, 1917, i, Ref. 2.

Colloidal bismuth is obtained by reducing the nitrate by stannous chloride in the presence of ammonia and ammonium citrate,[1] or the oxychloride by hypophosphorous acid.[2]

Bismuth serves for the preparation of many pharmaceutical products and cosmetics, and is also employed for the manufacture of alloys of low melting point, and in the construction of thermopiles.

460 *Alloys of Bismuth.*—Bismuth forms a number of alloys of low melting point, which are known by the general name of fusible metal. The temperature of the melting point depends on the proportion of the constituents, as is shown in the following table:

	Newton's Metal.	Rose's Metal.	Lichtenberg's Metal.	Wood's Metal.	Lipowitz.
Bismuth	8	2	5	4	15
Lead	5	1	3	2	8
Tin	3	1	2	1	4
Cadmium	0	0	0	1	3
Melting point	94·5°	93·75°	91·6°	71°	60°

The melting point can be still further lowered by the addition of mercury. Fusible metal is now largely used for stereotyping, obtaining copies of wood-cuts, etc., and is not only valuable on account of its low melting point, but also because it expands considerably in the act of solidification, and thus gives a perfect cast; it is important to make the cast when the metal is so far cooled that it is beginning to be viscid. If any of these liquid alloys be poured into a glass vessel this flies to pieces when the metal cools. Bismuth is also used in the manufacture of solder, and the soldering can be effected under hot water when a few drops of hydrochloric acid have been added. Alloys of lead, tin, and bismuth mixed together in such proportion that the mixture fuses at some particular temperature above 100° serve as safety plugs for boilers and automatic sprinklers. Bismuth alloys, melting at a given temperature, are used for tempering steel; the pencils used for writing on the so-called metallic paper likewise consist of an alloy of bismuth.

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[1] Lottermoser, *J. pr. Chem.*, 1899, [2], **59**, 480.

[2] Gutbier and Hofmeier, *Zeit. anorg. Chem.*, 1905, **44**, 225.

Bismuth in very small quantities renders gold and silver brittle, and greatly diminishes the conductivity of copper for electricity.

Molten bismuth, to which 0·05 per cent. of tellurium has been added, solidifies to a minutely crystalline mass, entirely different in appearance, fracture, etc., from the pure metal.

When bismuth is treated with a solution of sodium in liquid ammonia a compound of the formula $BiNa_3$ is formed as a bluish-black mass, which takes fire in the air, and decomposes water with evolution of hydrogen.[1]

COMPOUNDS OF BISMUTH.

Bismuth and Hydrogen.

461 It has long been suspected that bismuth forms a volatile hydride, and its existence has now been demonstrated by Paneth and Winternitz.[2] A bismuth-magnesium alloy is prepared by heating equal weights of powdered bismuth and silicon-free magnesium in an iron crucible in a rapid stream of dry hydrogen. When this is dissolved in 4*N*-hydrochloric or sulphuric acid the evolved hydrogen contains traces of bismuth hydride, the presence of which may be established by a mirror test or a luminescence test. The former is made in the familiar Marsh's apparatus (see Vol. I. p. 717); the mirror obtained closely resembles an antimony mirror in appearance. The luminescence test is more delicate. The gas issuing from the Marsh's apparatus is ignited and a piece of pure calcium carbonate held in the flame on a platinum loop. The carbonate is allowed to cool, and then placed at the edge of the hydrogen flame, when a cornflower-blue luminescence is observed, due to bismuth, and visible in bright daylight.

Bismuth hydride is absorbed by water and dilute sulphuric acid to some extent; a better absorbent is silver nitrate solution. It is also absorbed by anhydrous calcium chloride and soda-lime, and to a considerable extent by sodium carbonate and potassium hydroxide solutions. It is completely decomposed by concentrated sulphuric acid.

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[1] Joannis, *Compt. rend.*, 1892, **114**, 585.

[2] Paneth, *Ber.*, 1918, **51**, 1704; Paneth and Winternitz, *Ber.*, 1918, **51**, 1728; Paneth, *Chem. Zeit.*, 1920, **44**, 341; *Zeit. Elektrochem.*, 1920, **26**, 452; Paneth, Matthies and Schmidt-Hebbel, *Ber.*, 1922, **55**, [*B*], 775.

BISMUTH AND OXYGEN.

Only two well-defined oxides of bismuth are known:

Bismuth suboxide or dioxide, BiO or Bi_2O_2.
Bismuth trioxide, Bi_2O_3.

The suboxide has only very feeble basic properties, whereas the trioxide is a well-marked, basic oxide and corresponds to the stable salts of bismuth of the general formula BiR^{I}_3. Higher oxides are formed by the oxidation of the trioxide, to which the formulæ Bi_2O_4 and Bi_2O_5 have been ascribed.

Bismuth Suboxide, BiO.—The question as to the existence of an oxide of this composition has given rise to much discussion,[1] but the experimental evidence renders it probable that the suboxide is a definite chemical substance.

The suboxide was first described by Berzelius. It is best obtained by gently heating basic bismuth oxalate, $(BiO)_2C_2O_4$, in absence of air (Tanatar):

$$(BiO)_2C_2O_4 = 2BiO + 2CO_2,$$

or by carefully adding an alkaline solution of stannous hydroxide (1 mol.) to bismuth hydroxide (1 mol.) suspended in dilute potash, washing the suboxide first with dilute potash in absence of air until all traces of stannic oxide are removed, then washing with water, and finally drying at 120° in a current of carbon dioxide (Schneider). It is a black powder which is stable in the air and has the specific gravity 7·2, this being considerably less than that of a mixture of bismuth and its oxide having the same percentage composition as the suboxide (8·9). When heated in the air it passes into the trioxide with incandescence, and in absence of air is converted into a mixture of bismuth and bismuth oxide.

The suboxide is converted by hydrochloric acid into bismuth chloride, which dissolves, and insoluble metallic bismuth. The heat evolved in this reaction is considerably less than that produced when a corresponding amount of the trioxide is dissolved, and this affords a further proof of the individuality of the suboxide (Tanatar). It reduces Fehling's solution and potassium permanganate, and is converted by excess of alkaline stannous chloride into metallic bismuth.

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[1] Vanino and Treubert, *Ber.*, 1898, **31**, 1113, 2267; 1899, **32**, 1072; where the older literature is quoted. See also Schneider, *J. pr. Chem.*, 1898, [2], **58**, 562; 1899, [2], **60**, 524; Tanatar, *Zeit. anorg. Chem.*, 1901, **27**, 437; Herz and Guttmann, *Zeit. anorg. Chem.*, 1907, **53**, 63; Vanino and Zumbusch, *Arch. Pharm.*, 1910, **248**, 665; Herz, *Zeit. anal. Chem.*, 1915, **54**, 103, 413; Treubert and Vanino, *ibid.*, 1914, **53**, 564; 1915, **54**, 255.

Bismuth Trioxide, Bi_2O_3, is found as bismuth ochre in Cornwall, Virginia, Siberia, and Erzgebirge, as a yellow or greenish-grey, amorphous mass or as a powder, and it usually contains ferric oxide and other impurities. In order to prepare it artificially, the hydroxide, carbonate, or nitrate is heated Thus obtained, it is a yellow powder having a specific gravity of 8·2. It fuses at 820°, forming a brown liquid, and when this is allowed to cool the solid which is first formed passes at 704° with evolution of heat into a second modification, which forms a yellow, crystalline mass. When fused in porcelain a third form is produced which crystallises in long, yellow needles of specific gravity 8·55.[1] When a boiling solution of a bismuth salt is precipitated with potash the trioxide is obtained in microscopic needles, and if this be melted with caustic potash the product is found to crystallise in rhombic prisms. When the oxide is prepared by adding potassium cyanide to bismuth nitrate solution, boiling and heating the resulting grey powder in the air, it crystallises in tetrahedra belonging to the regular system.[2] It is therefore isodimorphous with antimony oxide.[3] The oxide prepared by roasting the metal appears to have been employed as a yellow paint in Agricola's time.

Bismuth trioxide is a stronger base than the corresponding oxide of antimony, and forms a well-defined series of salts, which are characterised by the ease with which they are converted by water into insoluble basic salts.

Bismuth Trihydroxide, $Bi(OH)_3$, is obtained as a white, amorphous powder by precipitating a bismuth salt with cold caustic soda or ammonia. It is soluble in caustic potash in the presence of glycerol,[3] and when precipitated from this solution by acids is free from basic salts, which are always present in the hydroxide prepared by precipitation with alkalis.[4] When dried at 100°, it has the composition Bi_2O_3,H_2O or $BiO{\cdot}OH$.

Higher Oxides of Bismuth.—When a current of chlorine is passed into a boiling solution of caustic potash or soda containing bismuth hydroxide in suspension, a red powder separates out which contains alkali and yields chlorine on boiling with hydrochloric acid. Under varying conditions, the nature of the products obtained in this reaction also varies and substances described as bismuth tetroxide, Bi_2O_4, a brown powder, and the dihydrate of this oxide, $Bi_2O_4.2H_2O$, an orange-yellow powder, have also been prepared by means of it. Similar highly oxidised products are formed by the electrolytic oxidation of the trioxide, and by the action of persulphates, of hydrogen peroxide, and of potassium ferricyanide on the trioxide in the presence of alkali.[1] According to Gutbier and Bünz,[2] none of these reactions leads in any case to a definite homogeneous product.

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[1] Gürtler, *Zeit. anorg. Chem.*, 1903, **37**, 222.

[2] Muir and Hutchinson, *Journ. Chem. Soc.*, 1889, **55**, 143.

[3] Löwe, *Zeit. anal. Chem.*, 1883, **22**, 498.

[4] Thibault, *J. Pharm.*, 1900, [6], **12**, 559.

Worsley and Robertson,[3] however, claim that definite oxides may be obtained. Using 5–10 per cent. sodium hydroxide and oxidising with chlorine, the only product is *bismuth tetroxide*, Bi_2O_4, which is freed from trioxide and alkali by repeated grinding with glacial acetic acid. Two forms of the anhydrous oxide exist, brown and purplish-black in colour, and also two similarly coloured forms of the monohydrate, Bi_2O_4,H_2O. All are soluble in nitric acid, sp. gr. 1·2, with liberation of oxygen, and decompose at 160°. When concentrated alkali solution is used, a yellow dihydrate, $Bi_2O_4,2H_2O$, is formed together with a red *pentoxide*, Bi_2O_5,H_2O. When ammonium persulphate or potassium ferricyanide are used as oxidising agents, the product is the tetroxide when the reaction proceeds in boiling dilute alkali, but with concentrated alkali a small amount of a *hexoxide*, Bi_2O_6, is also formed, which may be separated from the tetroxide owing to its insolubility in nitric acid, sp. gr. 1·2. The hexoxide is an anhydrous, pale brown powder which slowly loses oxygen and darkens in colour at the ordinary temperature.

BISMUTH AND THE HALOGENS.

462 *Bismuth sub-iodide*, BiI_2, is a volatile substance, crystallising in red orthorhombic needles.[4] The *sub-oxyiodide*, $2BiI_2,3BiO$, is non-volatile and begins to decompose at 350°.

Bismuth Trifluoride, BiF_3, is obtained as a white powder by dissolving the oxide in hydrofluoric acid and evaporating the solution. An *oxyfluoride*, BiOF, is formed when the acid is completely neutralised by the oxide. The fluoride forms a double salt with ammonium fluoride, BiF_3,NH_4F.[1]

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[1] See Deichler, *Zeit. anorg. Chem.*, 1899, **20**, 81, where a critical discussion of the earlier literature will be found. Muir, *Journ. Chem. Soc.*, 1887, **51**, 77; Hollard, *Compt. rend.*, 1903, **136**, 229; Hauser and Vanino, *Zeit. anorg. Chem.*, 1904, **39**, 381; Aloy and Frébault, *Bull. Soc. chim.*, 1906, [3], **35**, 396; Moser, *Zeit. anorg. Chem.*, 1906, **50**, 33.

[2] *Zeit. anorg. Chem.*, 1906, **48**, 162, 294; **49**, 432; **50**, 210; 1907, **52**, 124; *Chem. Centr.*, 1909, i., 732.

[3] *Trans. Chem. Soc.*, 1920, **117**, 63.

[4] Denham, *J. Amer. Chem. Soc.*, 1921, **43**, 2367.

Bismuth Dichloride, $BiCl_2$, is said to be formed when a slow current of chlorine is passed over the fused metal, or when the metal is heated with calomel to 250° or fused with the trichloride. Thermal investigation of the system Bi–$BiCl_3$, however, does not indicate the formation of any dichloride, but shows that within certain limits the metal and its trichloride form mixed crystals.[2]

Bismuth Trichloride, $BiCl_3$, was first prepared by Boyle[3] by heating bismuth with corrosive sublimate. It is also formed when the metal is burnt in a stream of chlorine, or when a concentrated solution of the oxide in hydrochloric acid is distilled, the receiver being changed after all the water has come over. Bismuth trichloride is a granular, white mass, which melts at from 225° to 230°, boils at 435° to 441°, and yields a vapour having the normal specific gravity of 11·35 (Jaquelain). Heated in a current of hydrogen, it is reduced to dichloride.[4] It forms a syrupy liquid when dissolved in a small quantity of water, though a larger quantity of water decomposes it, with formation of *bismuth oxychloride*, BiOCl, as a pure white powder, insoluble in water, but readily soluble in acids. It separates from a hot acid solution in tetragonal crystals[5] of the sp. gr. 7·717 at 15°, and is decomposed by excess of caustic potash.[6] Heated in air, bismuth oxychloride loses chlorine and takes up oxygen; in absence of air it becomes yellow-coloured, fusing without decomposition.

When a solution of the oxide in an excess of hydrochloric acid is evaporated, fine, needle-shaped crystals are deposited, having the composition $BiCl_3,2HCl$, whilst at 0° a saturated solution of the two deposits crystals of the compound $2BiCl_3,HCl,3H_2O$ which are stable at the ordinary temperature.[7] Bismuth trichloride forms double salts with the chlorides of the alkali metals,[1] the chlorides of many bivalent metals,[2] and with many organic bases. Ammonia yields three compounds—$BiCl_3,3NH_3$, a very volatile, colourless substance; $BiCl_3,2NH_3$, a dirty-grey, non-volatile mass; and $2BiCl_3,NH_3$, a red, crystalline body. They combine with hydrochloric acid to form double salts, which are also obtained when ammonium chloride is added to the solution of bismuth in the right proportion and the mixture evaporated.[3]

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[1] Helmholt, *Zeit. anorg. Chem.*, 1892, **3**, 115. See also Muir, Hoffmeister and Robbs, *Journ. Chem. Soc.*, 1881, **39**, 33.

[2] Marino and Becarelli, *Atti R. Accad. Lincei*, 1915, [5], **24**, ii, 625; 1916, [5], **25**, i, 105, 171, 221, 326.

[3] *Experiments and Considerations Touching Colours.*

[4] Muir, *Journ. Chem. Soc.*, 1876, i., 144.

[5] de Schulten, *Bull. Soc. chim.*, 1900, [3], **23**, 156.

[6] Herz and Muhs, *Zeit. anorg. Chem.*, 1904, **39**, 115.

[7] Engel, *Compt. rend.*, 1888, **106**, 1797.

Bismuth trichloride combines also with nitric oxide[4] to form the yellow compound $2BiCl_3,NO$, and with nitrosyl chloride[5] to form an orange-coloured powder, $BiCl_3,NOCl$.

Bismuth Tribromide, $BiBr_3$.—When bromine vapour is passed over powdered bismuth an energetic reaction takes place and a red liquid volatilises. This cools to a golden-yellow, glistening, deliquescent, crystalline mass, which melts at 210° and boils at 453°. Bismuth tribromide crystallises from ether in prisms, and water decomposes it into the white insoluble *oxybromide*, $BiOBr$. It forms crystalline double salts with the bromides of the alkali metals and also with the cyanides of various metals:[6] with ammonia it yields compounds similar to those of the chloride.

Bismuth Tri-iodide, BiI_3, is obtained by treating the powdered metal with iodine and heating the product; by precipitating a bismuth salt with potassium iodide solution, dissolving in hydriodic acid, and reprecipitating with water; or, better, by adding bismuth oxide to a solution of iodine in stannous chloride saturated with hydrochloric acid.[7] It sublimes in greyish-black, metallic, glistening, six-sided tablets, which are not decomposed by cold water, though they are converted by hot water into an insoluble oxyiodide. If a solution of the iodide in hydriodic acid be evaporated, rhombic pyramids of $BiI_3,HI,4H_2O$ are deposited. Bismuth iodide forms a large number of double salts.[8]

Bismuth Oxyiodide, $BiOI$, is obtained by decomposition of the tri-iodide with boiling water, or by heating the same in the air,[1] as a copper-red, crystalline mass, which can be sublimed when heated in the absence of air, but is gradually converted in presence of air into a crystalline oxide.

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[1] See Brigham, *Amer. Chem. J.*, 1892, **14**, 164; Field, *Journ. Chem. Soc.*, 1893, **63**, 540; Aloy and Frébault,, *Bull. Soc. chim.*, 1906, [3], **35**, 390.

[2] Weinland, Alber, and Schweiger, *Arch. Pharm.*, 1916, **254**, 521.

[3] Dehérain, *Compt. rend.*, 1862, **54**, 924.

[4] Thomas, *Compt. rend.*, 1895, **121**, 128.

[5] Sudborough, *Journ. Chem. Soc.*, 1801, **59**, 662.

[6] Vournazos, *Compt. rend.*, 1921, **172**, 535.

[7] Birckenbach, *Ber.*, 1907, **40**, 1404.

[8] Nicklès, *Compt. rend.*, 1860, **50**, 872; *J. Pharm.*, [3], **39**, 116; Linau, *Pogg. Ann.*, 1860, **111**, 240; Wells and Foote, *Amer. J. Sci.*, 1897, **3**, 461; Pfeiffer, *Zeit anorg. Chem.*, 1902, **31**, 191; Canneri and Perina, *Gazz.*, 1022, **52**, i., 241.

Bismuth and the Elements of the Sulphur Group.

463 *Bismuth Subsulphide*, BiS, was first described by Werther[2] and Lagerjhelm[3] as a grey, metallic, lustrous mass of needle-shaped crystals, obtained by fusing bismuth with sulphur and cooling quickly, but this contained free bismuth and the sulphide, Bi_2S_3. The existence of the same compound has been deduced by Pélabon,[4] but denied by Aten,[5] from the study of the equilibrium curve for bismuth and sulphur and the behaviour of these two elements in the presence of hydrogen.

Bismuth Trisulphide, Bi_2S_3, occurs as bismuthite in rhombic crystals, and also massive with a foliated or fibrous structure; its specific gravity is 6·4. It is found at Brandy Gill, Carrock Fells in Cumberland, at Redruth and Botallack and other localities in Cornwall, in the Erzgebirge, in Bolivia, and in other places. It is obtained artificially by fusing the metal with an excess of sulphur, or by precipitating a solution of bismuth chloride with sulphuretted hydrogen or sodium thiosulphate. Thus prepared, it forms a blackish-brown precipitate easily soluble in nitric acid and in boiling concentrated hydrochloric acid, but not in alkalis. Its solubility in pure water has been found by the conductivity method to be $0{\cdot}35 \times 10^{-6}$ gram-molecules (0·2 mgm.) per litre. When it is heated to 200° in a solution of an alkali it becomes crystalline, assuming the form of bismuthite, and when heated in the electric furnace yields metallic bismuth.[6]

The amorphous sulphide dissolves in potassium sulphide solution and very sparingly in sodium sulphide solution,[7] and forms salts of the formulæ Bi_2S_3,K_2S and Bi_2S_3,Na_2S when it is fused with sulphur and an alkali carbonate.[1]

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[1] Compare Dubrisay, *Compt. rend.*, 1909, **149**, 451.

[2] *J. pr. Chem.*, 1842, **27**, 65.

[3] *Schweiggers Journ.*, 1816, **17**, 416.

[4] *Ann. Chim. Phys.*, 1902, [7], **25**, 365; *J. Chim. phys.*, 1904, **2**, 321; *Compt. rend.*, 1903, **137**, 648, 920.

[5] *Zeit. anorg. Chem.*, 1905, **47**, 380. Compare Schneider, *Pogg. Ann.*, 1856, **97**, 480; Herz and Guttmann, *Zeit. anorg. Chem.*, 1907, **53**, 63; 1908, **56**, 422.

[6] Mourlot, *Compt. rend.*, 1897, **124**, 768.

[7] Ditte, *Compt. rend.*, 1895, **120**, 186. See also *J. Amer. Chem. Soc.*, 1896, **18**, 683, 1091.

Bismuth Oxysulphides.—The compound Bi_4O_3S occurs as karelilinite at the Savodinck Mine in the Altai; it is a crystalline mass having a strongly metallic lustre.

Bismuth Chlorosulphide, BiSCl, is obtained by fusing together in the air 1 part of sulphur and 8 parts of ammonium bismuth chloride, or by heating the latter compound in a current of sulphuretted hydrogen (Schneider), and also when the chloride is heated in dry sulphuretted hydrogen or the sulphide in dry chlorine. It is a reddish-brown solid, not decomposed by water. The corresponding *sulphobromide* is obtained similarly, whereas the *sulphiodide* can be prepared only by heating bismuth iodide with the trisulphide. All three compounds are decomposed by sulphuretted hydrogen at a bright red heat.[2]

Bismuth Trisulphate, $Bi_2(SO_4)_3$, is obtained as an amorphous, white mass by dissolving the metal or the sulphide in concentrated sulphuric acid and evaporating. This salt is decomposed by water with formation of the basic salt, $Bi_2O_3,SO_3,2H_2O$. When this is heated it loses water, and on cooling a yellow mass, consisting of Bi_2O_3,SO_3, is obtained. This salt is also obtained by heating the other sulphates. Another of these basic salts has the composition $Bi_2O_3,2SO_3,3H_2O$, and is obtained in small needles by acting upon the nitrate with sulphuric acid. Several other basic salts have also been described.[3] Concentrated sulphuric acid yields the acid salt, $Bi_2O_3,4SO_3$, several hydrates of which have been obtained.[4]

Bismuth Thiosulphate.—Complex thiosulphates are obtained by the addition of the alkali thiosulphates to bismuth chloride solution. The *potassium* salt, $K_3Bi(S_2O_3)_3,\frac{1}{2}H_2O$, is sparingly soluble in water, and the solution rapidly decomposes, bismuth sulphide being deposited. This solution does not react with iodine. The *sodium, ammonium,* and *strontium* salts are also known.[5]

464 *Bismuth Triselenide*, Bi_2Se_3, is obtained by fusing the elements together as a metallic, lustrous, brittle, crystalline

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[1] Schneider, *Pogg. Ann.*, 1869, **138**, 460.

[2] Muir and Eagles, *Journ. Chem. Soc.*, 1895, **67**, 90.

[3] See Allan, *Amer. Chem. J.*, 1902, **27**, 284.

[4] Adie, *Proc. Chem. Soc.*, 1899, **15**, 226.

[5] Carnot, *Compt. rend.*, 1876, **83**, 338; Hauser, *Zeit. anorg. Chem.*, 1903, **35**, 1. Vanino and Mussgnug, *Arch. Pharm.*, 1919, **257**, 264.

mass, having a specific gravity of 6·82, which is attacked only by nitric acid and aqua regia.

Bismuth Tritelluride, Bi_2Te_3, occurs as the mineral tetradymite, in which some of the tellurium is replaced by sulphur. It forms pale metallic steel-grey rhombohedra, or foliated or granular masses having a specific gravity of 7·2 to 7·9. Groth[1] considers this mineral to be an isomorphous mixture of the elements, as it is not isomorphous with bismuthite, Bi_2S_3, and as bismuth and tellurium can be fused together in all proportions.[2] Other bismuth tellurides of varying composition have been described, some of which occur as minerals. According to Mönkemeyer[3] only one stable compound of these two elements exists, namely, Bi_2Te_3, which melts at 573°.

BISMUTH AND THE ELEMENTS OF THE NITROGEN GROUP.

***465** *Bismuth Nitride*, BiN, is formed as a brown precipitate when bismuth iodide dissolved in liquid ammonia is added to a solution of potassamide in the same solvent.[4]

Bismuth Trinitrate, $Bi(NO_3)_3,5H_2O$, is obtained in large, transparent, triclinic prisms by dissolving the metal in nitric acid and evaporating the solution, which corrodes paper, and must, therefore, be filtered through asbestos or pounded glass. The crystals, which are deliquescent, are decomposed on heating, losing their water, and then leaving a residue, first of basic salt, and lastly of the trioxide. Hydrates with 2 and $1\frac{1}{2}H_2O$ also exist.[5]

Bismuth nitrate is isomorphous with the nitrates of yttrium, lanthanum, and others of the rare earth metals,[6] and forms double salts which are isomorphous with the corresponding salts of the rare earths and have been utilised in the fractional crystallisation of mixtures of these.[7]

When hydrated bismuth nitrate is ground with mannitol and water added, a clear solution is formed which is not precipitated on dilution and serves as a means of preparing many insoluble bismuth salts by double decomposition.[1]

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[1] *Tabell. Uebersicht d. Mineralien*, p. 12 (Braunschweig, 1882, Vieweg).

[2] See also Amadori, *Atti R. Accad. Lincei*, 1915, [5], **24**, ii, 200; 1918, [5], **27**, i. 131.

[3] *Zeit. anorg. Chem.*, 1905, **46**, 415. See also Gutbier, *ibid.*, 1902, **31**, 331.

[4] Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

[5] van Bemmelen and Rutten, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 196.

[6] Bodman, *Ber.*, 1898, **31**, 1237; *Zeit. anorg. Chem.*, 1901, **27**, 254; *Zeit. Kryst. Min.*, 1902, **36**, 192.

[7] Urbain, *Compt. rend.*, 1903, **137**, 568; *J. Chim. phys.*, 1906, **4**, 105.

Basic Bismuth Nitrate, $Bi(OH)_2NO_3$.—Libavius was aware that the solution of bismuth in nitric acid is precipitated by water, and Lemery, who describes the preparation of this compound, states that water containing common salt should be employed for this precipitation, pure water precipitating it, but much more slowly; and he adds that the product obtained weighs more than the metal employed. The reason of this, he explains, is that a certain quantity of spirit of nitre remains behind even if the precipitate be well washed. Boyle states that the solution of bismuth in aqua-fortis is almost completely precipitated by common water. In spite of this, many chemists, looking at the analogy between lead and bismuth, believed that salt water was necessary for the precipitation; indeed, the substance was for some time termed horn-bismuth. This error was definitely rectified by Pott, in 1739.

Basic nitrate of bismuth, formerly termed *magistery of bismuth*, is used as an important medicine, and many different receipts are given for its preparation. According to the method formerly prescribed in the British Pharmacopœia (1874), *bismuth subnitras* is best obtained by dissolving 2 parts by weight of bismuth in a mixture of 4 parts of nitric acid of specific gravity 1·42 with 3 parts of water. The clear liquid is poured off from any insoluble matter and evaporated to the point at which it occupies two volumes, and this is then poured into 80 parts of distilled water. The clear liquid is then decanted and the precipitate well stirred up with 80 parts of water, collected on a filter, and dried at a temperature not higher than 55°. The German and French pharmacopœias recommended somewhat similar processes. In all these methods a considerable quantity of bismuth remains in solution, and this may be obtained, as the hydroxide, by precipitating with ammonia. The bismuth is completely precipitated when 50,000 parts of water are present to one of the nitrate.[2]

Basic bismuth nitrate is a crystalline powder which reddens moistened litmus paper. Its composition varies somewhat according to the quantity of water used in the preparation, and a large number of basic salts have been described, the conditions of formation and existence of which have been investigated by van Bemmelen and Rutten,[1] by Allan,[2] and by de Schulten.[3] When washed for a long time it becomes more basic, until at last the hydroxide is left.

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[1] Vanino and Hauser, *Zeit. anorg. Chem.*, 1901, **28**, 210; *J. pr. Chem.*, 1906, [2], **74**, 142.

[2] Antony and Gigli, *Gazz.*, 1898, **28**, i., 245.

Basic bismuth nitrate is largely used as a medicine in cases of chronic diarrhœa and cholera. It is also employed in considerable quantities as a cosmetic; and this use is due to Lemery, who recommends it for softening the skin. When utilised for this purpose it was first termed *blanc d'Espagne,* which name, however, served to designate many other white pigments. Another name for this cosmetic is *blanc de fard.*

The basic nitrate, as well as the oxide, is also used for giving a colourless, iridescent glaze to porcelain. This is obtained by rubbing up basic nitrate with resin and gently heating the mixture with lavender oil, and can be coloured by the addition of oxides, such as oxide of chromium, which gives to it a sulphur or lemon-yellow colour. With addition of 5 per cent. of gold to the oxide of bismuth, a splendid copper-red colour with a reflected golden lustre is obtained. When a smaller quantity is employed, the glaze assumes a violet or pure blue colour, whilst with another treatment a rose-red tint is obtained. These glazes are also used in glass-staining.

466 *Bismuth Orthophosphate,* $BiPO_4$, is precipitated when solutions of bismuth nitrate and phosphoric acid are brought together in presence of nitric acid. When slowly precipitated by water from acid solution it forms microscopic crystals of sp. gr. 6·323 at 15° (de Schulten). In the same way, an insoluble *pyrophosphate,* $Bi_3(P_2O_7)_3$, is prepared with pyrophosphoric acid. When the oxide and phosphorus pentoxide are fused together, a clear glass is obtained, which on slow cooling becomes crystalline, and probably consists of the tetrametaphosphate.

Bismuth Arsenate, $Bi_4(As_2O_7)_3$, is a white precipitate insoluble in water and nitric acid, but soluble in hydrochloric acid. The *ortho-arsenate,* $BiAsO_4$, forms monoclinic prisms of sp. gr. 7·142 at 15° (de Schulten).

Phosphorus and *arsenic* do not readily combine with bismuth. The first of these forms a compound with molten bismuth, and if a current of phosphine be passed through a solution of bismuth, a black phosphide is precipitated, which, however, decomposes in absence of air into its elements. An alloy of bismuth and arsenic gives up the whole of the latter when heated.

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[1] *Proc. K. Akad. Wetensch. Amsterdam,* 1900, **3**, 196.

[2] *Amer. Chem. J.,* 1901, **25**, 307.

[3] *Bull. Soc. chim.,* 1903, [3], **29**, 720.

Arsine produces a black precipitate in bismuth solutions which behaves in a precisely similar way.

BISMUTH AND THE ELEMENTS OF THE CARBON GROUP.

467 *Basic Bismuth Carbonate*, $2(BiO)_2CO_3.H_2O$, is obtained as a white powder when ammonium carbonate is poured into a solution of bismuth nitrate and the precipitate dried at a gentle heat. It is employed as a medicine. At 100° it loses water; stronger heating converts it into the trioxide.

The mineral bismuthite, $3(BiO)_2CO_3,2Bi(OH)_3,3H_2O$, is another basic carbonate and is found at Schneeberg, at Chesterfield, South Carolina, and at other places, together with bismuth ores. It is a white or siskin-green, earthy mass, and sometimes occurs in acicular pseudomorphous crystals.

Bismuth Silicate, $Bi_4(SiO_4)_3$, is found as eulytite in small, glistening yellow or brown regular tetrahedra and occurs in the Erzgebirge together with phosphates of iron and manganese.

DETECTION AND ESTIMATION OF BISMUTH.

468 When a bismuth compound is heated in the upper reducing flame of the Bunsen burner on an asbestos thread, a cold porcelain dish, held above it, receives a brown or black deposit of metallic bismuth, which is only slowly dissolved by cold dilute nitric acid. A brittle metallic bead is obtained when the compound is heated on the carbonised match, and this dissolves in nitric acid, yielding a brown precipitate of bismuth with excess of stannous chloride and caustic soda. A characteristic reaction of the bismuth salts is the precipitation of the blackish-brown sulphide with sulphuretted hydrogen, insoluble in ammonium sulphide, and easily soluble in nitric acid. In addition to this, water produces, in solutions which are not too strongly acid, a white precipitate of an insoluble basic salt, and ammonia throws down a white precipitate of the hydroxide insoluble in excess. These reactions serve to separate bismuth from other metals, as well as to detect its presence. If other metals precipitable by sulphuretted hydrogen are present, the washed precipitate is first digested with ammonium sulphide, in order to separate arsenic, antimony, and tin. The precipitate is then well washed, dissolved in nitric acid, and dilute sulphuric acid added to the filtrate to separate lead; the precipitate is filtered off, and an excess of ammonia added which throws down the

bismuth as the hydroxide, whilst any copper or cadmium present remains in solution. The precipitate is dissolved in a small quantity of hydrochloric acid, the liquid concentrated by evaporation, and added to a large quantity of water, when the insoluble oxychloride is precipitated. Care must be taken that all the antimony is removed by long digestion of the sulphides with ammonium sulphide, and the residue well washed with water, for otherwise an insoluble oxychloride of antimony may be precipitated and mistaken for bismuth.

Bismuth can be estimated in several ways. If the solution contains the nitrate only, it may be precipitated with ammonium carbonate, heated for some time almost to boiling, filtered, the precipitate dried and converted by ignition into the trioxide, which is weighed. If other acids are present, the bismuth is precipitated by sulphuretted hydrogen, the washed precipitate dissolved in nitric acid, and treated as above; or it may be dried, excess of sulphur removed by carbon disulphide, and the residual sulphide dried at 100° and weighed. The phosphate may also be precipitated in the presence of phosphoric acid or dilute nitric acid, ignited, and weighed.[1] If the solution of the nitrate contains only a small quantity of free acid it may be precipitated with potassium dichromate, or with arsenic acid, and the precipitate dried and weighed. Bismuth may also be estimated as the metal by reduction with potassium cyanide. The metallic mass is well washed with water and alcohol, and weighed after drying. Bismuth may also be separated electrolytically from an acid solution of the nitrate in the presence of alcohol, glycerol, or acid potassium sulphate.[2]

The Atomic Weight of bismuth has been determined by several chemists, but without very concordant results. In 1851 Schneider,[3] by converting the metal into the oxide, obtained the number 208·05, and this was confirmed in 1883 by Löwe,[4] who used the same method and obtained the number 207·8, and by Marignac,[5] who, in 1883, found the atomic weight to be 208·16 by converting the oxide into the sulphate. Dumas,[6] on the other hand, in 1859, by the analysis of the chloride, obtained the number 210·7, which is certainly too high, and Marignac, by analysing the oxide, obtained the value 208·6. In 1890 Classen[1] made a series of nine concordant experiments in which carefully purified bismuth was converted into the oxide and found the number 208·9. Schneider, in 1894,[2] repeated his experiments and again obtained the number 208·05. The lower determinations have been confirmed by the results obtained by Gutbier[3] and his co-workers, who obtained the values 208·02—208·15 by converting the metal into oxide, reducing the oxide to metal, converting the metal into sulphate, and determining the ratio $BiBr_3 : AgBr$. The value 208·0 is therefore (1922) adopted. Nevertheless, it is possible that the higher results are more nearly correct, since Hönigschmid,[4] who has analysed the pure chloride with all modern precautions, has obtained the value 209·02.

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[1] Stähler and Scharfenberg, *Ber.*, 1905, **38**, 3862, 3943; *Chem. Zeit.*, 1907, **31**, 615.

[2] *Compt. rend.*, 1900, **131**, 179; *Zeit. anorg. Chem.*, 1901, **27**, 1; *J. Amer. Chem. Soc.*, 1903, **25**, 83; Richardson, *Zeit. anorg. Chem.*, 1913, **84**, 277.

[3] *Pogg. Ann.*, 1851, **82**, 303.

[4] *Zeit. anal. Chem.*, 1883, **22**, 498.

[5] *Zeit. anal. Chem.*, 1884, **23**, 120.

[6] *Ann. Chim., Phys.* 1859, [3], **55**, 177.

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[1] *Ber.*, 1890, **23**, 938.

[2] *J. pr. Chem.*, 1894, **56**, 461.

[3] *Zeit. Elecktrochem.*, 1905, **11**, 831; *J. pr. Chem.*, 1908, ii., **77**, 457; ii. **78**, 409, 421. See also the Dissertations (Erlangen) of Birckenbach, 1905; Mehl[illegible], 1905; and Janssen, 1906.

[4] *Zeit. Elektrochem.*, 1920, **26**, 403. See also Hönigschmid and Birckenbach, *Ber.*, 1921, **54**, [*B*], 1873; Classen and Ney, *Ber.*, 1920, **53**, [*B*], 2267.

GROUP VI.

Sub-group (*a*).	*Sub-group* (*b*).
Oxygen.	Chromium.
Sulphur.	Molybdenum.
Selenium.	Tungsten.
Tellurium.	Uranium.

469 In this group, as in Groups I, II, and III, the elements may be divided into two well-defined sub-groups, as shown in the above list, the sub-group (*a*) consisting of non-metallic elements (Vol. I), whilst those in the sub-group (*b*) are metals. Oxygen falls in the even series, and therefore strictly belongs to sub-group (*b*), but as in the case of glucinum in Group II, it is much more nearly allied to the members of the odd series.

Oxygen is gaseous at the ordinary temperature, whilst sulphur, selenium, and tellurium are solids, the melting and boiling points of which rise with increasing atomic weight. The elements of the chromium group melt only at high temperatures, and are reduced from their oxides with difficulty.

All the metals unite with the elements of the oxygen group to form oxides, sulphides, selenides, and tellurides; and the different series of compounds thus formed present strong analogies among themselves, as has already been seen in the description of the compounds of the metals of the previous groups. The analogy which exists between the "oxy-salts" obtained by the union of a basic and an acidic oxide, and the "thio-salts" formed in a similar manner from the acidic and basic sulphides, has also been frequently alluded to.

The most characteristic compounds formed by these elements (with, of course, the exception of oxygen) are the trioxides and their numerous derivatives. All these behave as acid-forming oxides, and give rise to well-defined series of compounds having the general formula $M^{I}_{2}R^{VI}O_{4}$, in which M^{I} represents hydrogen, or a univalent metal, and R^{VI} an element of the group under consideration. These possess strongly marked analogies with each other, and the salts of the same metal are as a rule isomorphous. These oxides also form salts containing from two to eight equivalents of the acidic oxide to one of basic oxide, such as the disulphates, $M^I_2O,2SO_3$, and dichromates, $M^I_2O,2CrO_3$, the trichromates, $M^I_2O,3CrO_3$, the octotungstates, $M^I_2O,8WO_3$, etc.

The constitution of the normal acids corresponding to the trioxides is represented by the formula $O_2R^{VI}(OH)_2$, and the hydroxyl groups in these acids may be replaced by negative radicles such as the halogens. The compounds thus formed from the elements of lower atomic weight, such as sulphur and chromium, are acidic chlorides, and are at once decomposed by water with formation of the acid; but as the atomic weight of the element increases, the basicity of the radicle $R^{VI}O_2$ also increases, and the compounds become more stable, until, in the case of uranium, the compounds formed by negative radicles with the group UO_2 constitute the most stable series of salts.

The elements of this group also form other oxides containing a less amount of oxygen than the trioxide; in the case of sulphur, selenium, and tellurium, these oxides (RO_2) are acidic or neutral, whilst with the metals of the chromium group (RO, R_2O_3, and RO_2) they are usually basic, and give rise to series of salts which often have strong reducing properties, owing to their tendency to unite with oxygen, forming derivatives of the trioxide.

The elements of sub-group (*a*) combine with hydrogen and the alkyl radicles forming volatile compounds; the elements of sub-group (*b*) do not form similar derivatives.

Oxygen is bivalent in almost all of its compounds, but possibly sometimes acts as a tetrad. The remaining elements are, as stated above, sexavalent in their most characteristic oxygen compounds, but the valency in their other compounds, especially with the halogens, varies very considerably; the elements sulphur, selenium, and tellurium are always bivalent towards hydrogen and the alkyl radicles, and usually either bi-, quadri- or sexa-valent in their other compounds, but no such regularity is observed in sub-group (*b*).

CHROMIUM. $Cr = 52{\cdot}0$. At. No. 24.

470 In 1762 Lehmann, in a letter to Buffon, "de nova mineræ plumbi specie crystalline rubra," described a new mineral from Siberia, now termed crocoisite. Vauquelin and Macquart investigated the composition of this mineral in 1789, and came to the conclusion that it contained lead, iron, alumina, and a large quantity of oxygen. However, when the former chemist re-investigated the subject in 1797, he found that the lead present was combined with a peculiar acid, which he recognised as the oxide of a new metal. To this the name of *chromium* was given, because its compounds are usually coloured (from *χρῶμα*, colour). Chromium was discovered in crocoisite simultaneously and independently by Klaproth.

Chromium is not a very common substance, and except for its occurrence in very small amounts in certain meteorites it is not found in the free state. It is found in several other minerals besides crocoisite or lead chromate, $PbCrO_4$, especially as chrome iron stone or chromite, FeO,Cr_2O_3, a mineral which is the chief ore of chromium and is the one usually employed for the manufacture of the chromium compounds. Deposits in Rhodesia and New Caledonia are of special economic importance, but the mineral occurs also in a number of localities in Europe, Asia Minor, North America, and New Zealand. Chromium is widely distributed amongst certain classes of rocks, *e.g.*, basalts, in many of which it occurs in small amounts. Chromitite, $(Fe,Al)_2O_3,2Cr_2O_3$, occurs as minute, lustrous crystals in the sand of some of the streams descending from the Kopaonik Mountains, Serbia.[1] Ceylonite, which occurs in Western Australia, contains nearly 23 per cent. of chromic oxide.[2] Uvarovite or chrome garnet is $3CaO,Cr_2O_3,3SiO_2$. Chromium also forms the colouring matter of several minerals; thus the green colour of emerald, as was shown by Vauquelin, is due to chromium; whilst serpentine, pennine, chromic mica or fuchsite, possibly sapphire,[3] and other minerals owe their colour to the same metal. Attempts to imitate the unique spectra of such natural substances have met with partial success only.[4]

Metallic chromium is obtained by the reduction of the oxide or chloride; thus Deville obtained it by strongly heating the oxide with sugar charcoal in a lime crucible,[5] and Wöhler by heating chromic chloride with zinc under a layer of sodium chloride, and treating the alloy of zinc and chromium thus obtained with nitric acid;[6] it then forms a grey powder consisting of minute octahedra.[7] Jäger and Krüss obtained the pure metal by this process in tin-white rhombohedra.[1] Magnesium and sodium have also been employed in place of metallic zinc, the first of these being specially suitable for a laboratory preparation.[2] If a mixture of chromic chloride with finely divided iron is heated at 700-1200°, ferric chloride is volatilised, and the metallic chromium remains in a finely divided form.[3] Another method of preparation is that of Moissan,[4] which consists in heating a mixture of chromium sesquioxide and carbon in the electric furnace; the first product contains large quantities of carbon, which is removed by first heating strongly with lime when the greater part of the carbon is converted into calcium carbide, and then eliminating the remainder by fusing the purified product in a crucible brasqued with the double oxide of calcium and chromium.

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[1] Jovitschitsch, *Monatsh.*, 1909, **30**, 39; *Bull. Soc. franç. Min.*, 1912 (1913), **35**, 511.

[2] Simpson, *Min. Mag.*, 1920, **19**, 99.

[3] Duboin, *Ber.*, 1898, **31**, 1977.

[4] Moir, *Trans. Roy. Soc. S. Africa*, 1918, **7**, 129.

[5] *Compt. rend.*, 1857, **44**, 673.

[6] *Annalen*, 1859, **111**, 230.

[7] Prinz, *Compt. rend.*, 1893, **116**, 392.

Metallic chromium is easily prepared from chromic oxide by the "thermite" process (p. 737), which consists in mixing finely divided aluminium with chromic oxide in slight excess of the equivalent proportion and igniting the mixture.[5]

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3.$$

When once started, the reduction proceeds rapidly with great evolution of heat, and produces a fused mass of metallic chromium of considerable purity. This is shown by the following analysis:[6] Cr 99·55 per cent., Fe 0·14 per cent., Si 0·31 per cent.

Metallic chromium finds its chief technical application in the form of its alloys; large quantities are used in the form of ferro-chrome, manufactured by the reduction of chromite in the electric furnace or by means of aluminium; these ferro-chromes generally contain between 60 and 70 per cent. of chromium. Chromium has also been prepared by the electrolysis of a warm solution of chromic chloride or of a cold solution acidified with hydrochloric acid, and is thus obtained as a bright silver-white deposit.[7] It can also be deposited from the violet solutions of chrome alum, but not from the green solutions.

Pure chromium is somewhat harder than glass, and has a melting point considerably higher than that of platinum, probably between 1520° and 1550°, whilst if it contains 1·5—3 per cent. of carbon it melts at a lower temperature, but can be cut only by the diamond. It may be distilled in the electric furnace.[1] The polished metal resembles iron, but is brighter and has a somewhat whiter colour: it has a density of 6·92 at 20°, a specific heat [2] of 0·1080 at 50°, and burns when heated in the oxy-hydrogen flame more brilliantly than iron. It is attacked by dilute hydrochloric acid, slowly in the cold and rapidly on heating, and also dissolves slowly in dilute sulphuric and nitric acids. With concentrated sulphuric acid it evolves sulphur dioxide, with formation of a deep-coloured solution, but it is unaffected by hot concentrated nitric acid; its rate of solution in acids is characterised by periodic variations. Chromium, like iron, has been found to exist in a "passive" state.[3] Colloidal chromium has also been prepared.[4]

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[1] *Ber.*, 1889, **22**, 2052.

[2] Glatzel, *Ber.*, 1890, **23**, 3127.

[3] Weber, U.S. Pat. 1373038.

[4] *Compt. rend.*, 1893, **116**, 349; 1894, **119**, 185; *Ann. Chim. Phys.*, 1896, [7], **8**, 559.

[5] *J. Soc. Chem. Ind.*, 1898, **17**, 543.

[6] *J. Iron Steel Inst.*, 1902, **1**, 185.

[7] Cowper-Coles, *Chem. News*, 1900, **81**, 16; Férée, *Bull. Soc. chim.*, 1901, [3], **25**, 617; Neumann, *Zeit. Elektrochem.*, 1901, **7**, 656; Carveth and others, *J. Physical Chem.*, 1905, **9**, 231, 353; *Zeit. Elektrochem.*, 1906, **12**, 329; Askenasy and Révai, *Zeit. Elektrochem.*, 1913, **19**, 344.

471 *Chromium Alloys.*—By far the most important are those with iron and nickel, since they are very resistant to corrosion, either with acids or by heating in the air. "Nichrome" wire of the average composition: 58—62 per cent. Ni; 8—4 per cent. Cr; 23—26 per cent. Fe; 0·5—2 per cent. Mn, Zn, SiO_2, and 0·2—1 per cent. C, is largely used as a resistance wire for electrically heated apparatus. "Stainless steel" is an iron–chromium alloy.[5]

Chromium Amalgams.—By electrolysis of chromic chloride under suitable conditions, using a mercury cathode, a solid chromium amalgam is obtained having the composition Hg_3Cr. Under pressure this loses mercury, yielding an amalgam of the composition HgCr. When either of these amalgams is heated in a vacuum at 300°, the whole of the mercury is driven off, leaving the chromium as a powder which is pyrophoric at the ordinary temperature, and also combines with nitrogen on heating.[6]

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[1] Moissan, *Compt. rend.*, 1906, **142**, 425.

[2] Schübel, *Zeit. anorg. Chem.*, 1914, **87**, 81. See also Jäger and Krüss, *Ber.*, 1889, **22**, 2028.

[3] Hittorf, *Zeit. physikal. Chem.*, 1898, **25**, 729; 1899, **30**, 481; Ostwald, *Zeit. physikal. Chem.*, 1900, **35**, 33, 204; Morgan and Duff, *J. Amer. Chem. Soc.*, 1900, **22**, 331; Brauer, *Zeit. physikal. Chem.*, 1901, **38**, 441; Döring, *J. pr. Chem.*, 1902, [2], **66**, 65; Bernoulli, *Physikal. Zeit.*, 1904, **5**, 632; Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 138.

[4] Kužel, Ger. Pat. 197379; Svedberg, "*Herstellung kolloider Lösungen anorganischer Stoffe*," 1909, p. 413.

[5] See Jänecke, *Zeit. Elektrochem.*, 1917, **23**, 49; Murakami, *Sci. Rep. Tôhoku Imp. Univ.*, 1918, **7**, 217.

[6] Férée, *Compt. rend.*, 1895, **121**, 822.

COMPOUNDS OF CHROMIUM.

CHROMIUM AND OXYGEN.

472 Chromium combines with oxygen to form the well-defined oxides, chromium sesquioxide, Cr_2O_3, and chromium trioxide, CrO_3. The former is a basic oxide, corresponding to the chief series of chromium salts, in which the metal is tervalent; whilst the latter is an acidic oxide, which combines with water to form chromic acid, H_2CrO_4, the salts of which resemble the corresponding sulphates, selenates, and tellurates, and are frequently isomorphous with them.

In addition to these, chromium monoxide, CrO, and the corresponding hydroxide have been prepared, and the latter yields with acids the *chromous* salts, in which the metal is bivalent. A number of other oxides have been described which may be regarded as combinations of one or other of the basic oxides with the trioxide; the best defined of these is chromium dioxide, which has really the constitution $Cr_2O_3 \cdot CrO_3 = 3CrO_2$, and will be described with the other chromates.

Chromium Monoxide, CrO.—An oxide of this composition is obtained as a black powder by the oxidation of chromium amalgam by exposure to air or by treatment with dilute nitric acid. It cannot, however, be obtained by direct reduction of the sesquioxide. When heated in air or when struck with a hammer it inflames and burns to the sesquioxide. It is insoluble in nitric acid, but dissolves in hydrochloric acid with liberation of hydrogen and formation of chromous and chromic chlorides.[1] By the action of hydrogen at 1000° it is reduced to the metal.

Chromous Hydroxide, $Cr(OH)_2$, is formed by the action of aqueous potash, freed from air, on chromous chloride solution, as a brownish-yellow precipitate, which is readily oxidised with evolution of hydrogen, and on drying in absence of air has a dark brown colour.[2] On ignition, it decomposes thus:

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

Chromium Sesquioxide, or *Chromic Oxide*, Cr_2O_3, occurs in the hydrated form as chrome ochre, and is obtained artificially as a dull green, amorphous powder by igniting the hydroxide or the trioxide, or by heating a mixture of potassium dichromate with sulphur or ammonium chloride, and lixiviating the residue. The colour of the oxide prepared by gently igniting mercurous chromate, Hg_2CrO_4, in a covered crucible is a very fine green. It melts at the temperature of the oxy-hydrogen blowpipe, solidifying to a crystalline, almost black mass. Chromic oxide is also obtained in the crystalline state by fusing the amorphous substance with calcium carbonate and boron trioxide, or by ignition in a stream of oxygen. Wöhler[1] considered that crystalline chromic oxide is formed by passing the vapour of chromyl dichloride, CrO_2Cl_2, through a red hot tube, but the product appears to contain a large though varying proportion of a magnetic oxide, Cr_5O_9.[2] Another method consists in heating potassium dichromate either alone, or, better, mixed with common salt; the ignited mass is dissolved in water, when chromic oxide remains in bright, iridescent spangles, which have a density of 5·01.[3]

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[1] Férée, *Bull. Soc. chim.*, 1901, [3], **25**, 619; Dieckmann and Hanf, *Zeit. anorg. Chem.*, 1914, **86**, 301. See also Field, *J. Ind. Eng. Chem.*, 1916, **8**, 238.

[2] Moberg, *J. pr. Chem.*, 1848, **43**, 114; **44**, 322; Péligot, *Compt. rend.*, 1844, **19**, 609, 734; *Ann. Chim. phys.*, 1844, [3], **12**, 528.

The amorphous oxide glows when heated at 500—610°;[4] after strong ignition it is almost insoluble in acids, and in order to bring it into solution it must either be heated for a long time with strong sulphuric acid, or fused with potassium hydrogen sulphate. The heats of formation of the various forms of chromic oxide exhibit striking differences.[5] Chromic oxide is used in the preparation of coloured glass, enamels, and porcelain, imparting to them a fine green tint. It forms one of the most permanent green pigments, known as chrome-green; it also finds limited application as a catalyst.

Chromic Hydroxides.—Pure chromic hydroxide, Cr_2O_3,xH_2O,[6] may be obtained by precipitation of boiling solutions of chromic salts, free from alkali, with ammonia. Several modifications are known; the first, which reacts directly with three equivalents of acid forming the normal chromic salts, is obtained by the action of alkalis on cold solutions of violet chromic salts, and has probably the constitution $Cr(OH)_3$. It is best prepared by adding ammonia to a solution of a violet chromic salt free from alkali, and forms a pale blue precipitate, which, after drying over sulphuric acid, has the composition $Cr(OH)_3,2H_2O$. When heated in a current of hydrogen at 200° it yields the hydroxide, $CrO(OH)$; some water is retained even on long heating in hydrogen at 420°,[1] but at a red heat it commences to glow strongly and passes into chromic oxide. A hydroxide of this composition, or Cr_2O_3,H_2O, has also been obtained as a brown substance by the electrolysis of neutral solutions of chromic chloride.[2] Another hydroxide, which has probably the constitution $Cr_2O(OH)_4$, is obtained by dissolving the first-named hydroxide in sodium hydroxide solution and reprecipitating with hydrochloric acid, and is also formed by the action of alkalis on the green chromic salts of oxy-acids (p. 1082); when treated with acids it reacts with only two equivalents of the latter, yielding the above green salts, which, however, on keeping in contact with acid gradually combine with it, forming the normal violet salts. Another hydroxide which behaves similarly is formed, according to Recoura, by the action of alkalis on the chromic oxychloride obtained by oxidation of chromous chloride solution. It differs from the foregoing in the amount of heat evolved by the action of two equivalents of acid.[3] Whilst chromic hydroxide, when freshly precipitated in the cold, is soluble in acids, it becomes insoluble when kept or heated.

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[1] *Annalen*, 1846, **60**, 203.

[2] Soné and Ishiwara, *Sci. Rep. Tôhoku Imp. Univ.*, 1914, **3**, 271; Wedekind and Horst, *Ber.*, 1915, **48**, 105.

[3] Schröder, *Pogg. Ann.*, 1859, **106**, 226; **107**, 113. See also Ditte, *Compt. rend.*, 1902, **134**, 336.

[4] Rothaug, *Zeit. anorg. Chem.*, 1913, **84**, 165; Endell and Rieke, *Zentr. Min. Geol.*, 1914, 246; Mixter, *Amer. J. Sci.*, 1915, [4], **39**, 295.

[5] Mixter, *loc. cit.*

[6] Weiser, *J. Physical Chem.*, 1922, **26**, 401, considers that an indefinite number of hydrous oxides exists.

Guignet's Green is obtained by fusing together potassium dichromate and crystallised boric acid in equal molecular proportions and lixiviating the fused mass with water. The residue after grinding is a fine green powder, and is largely used as a pigment. It is usually described as having the composition $Cr_2O(OH)_4$, but it always contains boric acid, and may possibly have the composition $3Cr_2O_3,B_2O_3,4H_2O$.

Colloidal Chromic Hydroxide.—Freshly precipitated and washed chromic hydroxide dissolves in aqueous chromic chloride, and on dialysing this solution Graham obtained a liquid containing 33 molecules of Cr_2O_3 to one of HCl. If the dialysis is carried out with hot liquids, much purer chromic hydroxide sols are obtained in a few hours instead of in as many weeks at the ordinary temperature.[4] The dark green solution does not undergo change on boiling or dilution, but at once coagulates on addition of the smallest quantity of a salt,[1] or slowly on merely *keeping* at the ordinary temperature. The precipitated colloid has no constant composition between 15° and 280°.[2] Violet and green jellies of chromic oxide can be produced by addition of caustic alkalis to stationary solutions of chromic salts containing a sufficient amount of sodium acetate.[3]

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[1] Mixter, *loc. cit.*

[2] Férée, *Bull. Soc. chim.*, 1901, [3], **25**, 620.

[3] *Ann. Chim. Phys.*, 1887, [6], **10**, 60.

[4] Neidle and Barab, *J. Amer. Chem. Soc.*, 1916, **38**, 1961; 1917, **39**, 71. See also Weiser, *loc. cit.*

Chromites.—Although the solubility of chromic hydroxide in aqueous alkalis is doubtless due largely to the action of the alkali in converting the gel into a true colloidal solution,[4] it must depend in part on the fact that, like alumina, chromic oxide acts as an acidic oxide towards strong bases, yielding salts termed the chromites.[5] Thus a green compound of chromic oxide with an alkali is thrown down on the addition of potash or soda to a solution of a chromic salt, and the alkali cannot be removed even by boiling water. This precipitate is, however, easily soluble in an excess of the precipitant, but can be again thrown down either by partial neutralisation with acids or by boiling the solution. When caustic soda is added to a solution of a chromic salt and a salt of magnesium (for instance), a precipitate is obtained of a compound of magnesia and chromic oxide which does not dissolve in an excess of alkali. In this way, "chromites" or "absorption compounds" of sodium, potassium, calcium, barium, magnesium, zinc, lead, iron, cobalt, nickel, copper, and cerium have been obtained, in a gelatinous condition, or their existence has been indicated by physical measurements. Their composition depends upon the conditions of their preparation.

The chromites may be obtained also by the action of boiling aqueous alkalis on the corresponding sulphochromites.

Better defined compounds are produced by fusion of the appropriate oxides, by strong ignition of metallic chromates, and by fusion of alkali chromates or dichromates with metallic chlorides. In this way, chromites of lithium, barium, calcium, magnesium, zinc, copper, cadmium, manganese, iron, and cobalt have been prepared.

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[1] Graham, *Phil. Trans.*, 1861, **151**, 183; Meunier, *J. Soc. Leather Trades Chem.*, 1921, **5**, 103.

[2] van Bemmelen, *Rec. trav. chim.*, 1887, **7**, 114. See also Biltz, *Ber.*, 1902, **35**, 4431; 1904, **37**, 1095; Paal, *Ber.*, 1914, **47**, 2211; and Picton and Linder, *J. Chem. Soc.*, 1897, **71**, 572; Lottermoser, *Über anorg. Kolloide*, Stuttgart, 1901; Siewert, *Z. ges. Nat.*, 1861, **18**, 244; van Bemmelen, *Die Absorption*, Dresden, 1910; Baikow, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 660; Reinitzer, *Monatsh.*, 1882, **3**, 249.

[3] Bunce and Finch, *J. Physical Chem.*, 1913, **17**, 769; Nagel, *ibid.*, 1915, **19**, 331, 569.

[4] Nagel, *loc. cit.*, Fischer and Herz, *Zeit. anorg. Chem.*, 1902, **31**, 352; 1904, **40**, 39; Bancroft, *Chem. News*, 1916, **113**, 113.

[5] Wood and Black, *J. Chem. Soc.*, 1916, **109**, 164.

Ferrous Chromite, $FeCr_2O_4$.—This occurs in nature as chromite or chrome iron ore, a mineral of the spinel group, $M''O,M'''_2O_3$, the proportions of ferrous oxide and chromic oxide exhibiting considerable variation within limits. Sometimes the composition approximates to $Fe_2Cr_2O_5,Fe_3Cr_4O_9$;[1] and alumina and magnesia frequently occur as isomorphous constituents. Chromite is rarely found crystallised in regular octahedra, generally occurring massive, with a granular, crystalline fracture. It is largely used in the manufacture of "neutral" refractory furnace-linings.

Chromous Chromite, CrO,Cr_2O_3,xH_2O.—This is stated to be a reddish-brown oxide, fairly stable in dry air.[2]

CHROMIUM TRIOXIDE, CHROMIC ACID, AND THE CHROMATES.

473 Chromic oxide is unchanged when heated alone in air; the hydroxide is not so stable, and in presence also of certain metallic oxides under appropriate conditions of pressure, oxygen is readily absorbed.[3] A mixture of chromic acid with an alkali or alkaline earth can be completely oxidised by oxygen at a red heat, whilst if oxygen is supplied to the alkali-fusion in the form of potassium nitrate or chlorate, the reaction takes place even more readily, yielding a yellow, soluble mass of an alkali chromate.

Alkaline solutions of chromic salts are easily oxidised to chromates by chlorine, bromine, hydrogen peroxide,[4] persulphates, and a number of other oxidising agents:

$$Cr_2O_3 + 10KOH + 3Br_2 = 2K_2CrO_4 + 6KBr + 5H_2O.$$

Acid solutions are also susceptible to oxidation, though less easily, by potassium permanganate, lead dioxide, manganese dioxide, ceric nitrate, and particularly by persulphates.[5]

Electrochemical oxidation of chromic salts can be so successfully carried out that this method is now largely used for the commercial regeneration of chromate solutions from the chromic salts into which they have become converted.[1]

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[1] Christomanos, *Ber.*, 1877, **10**, 343.

[2] Moberg, *J. pr. Chem.*, 1843, **29**, 175; Péligot, *Compt. rend.*, 1844, **19**, 609, 734; *Ann. Chim. Phys.*, 1844, [3], **12**, 528; Baugé, *Compt. rend.*, 1898, **127**, 551.

[3] Millbauer, *Chem. Zeit.*, 1916, **40**, 587.

[4] Bourion and Sénéchal, *Compt. rend.*, 1919, **168**, 59, 89.

[5] Salinger, *Zeit. anorg. Chem.*, 1903, **33**, 342.

The chromates are usually yellow, yellowish-red, or red in colour; basic salts are known, but acid salts do not appear to exist. The salts frequently termed acid salts are dichromates corresponding to the disulphates (pyrosulphates), and are salts of dichromic acid, $H_2Cr_2O_7$. Trichromates and other polychromates are also known.

Chromium Trioxide or Chromic Anhydride, CrO_3.—This compound is formed by the action of strong sulphuric acid on solutions of the chromates. According to Zettnow[2] the best yield is obtained when 300 grams of potassium dichromate are mixed with 500 c.c. of water, 420 c.c. of concentrated sulphuric acid added, and the mixture is kept for twelve hours in order that the potassium hydrogen sulphate may crystallise out. The mother-liquor is then heated to 80° or 90°, and 150 c.c. of sulphuric acid are added, together with enough water to dissolve the crystals of trioxide which at first separate out. After twelve hours the liquid is poured off from the crystals which have separated, and a second and a third crop may be obtained by concentration. The liquid is drained from the crystals, which are then washed on a pumice-stone or asbestos filter with pure nitric acid, of density 1·46, the adhering nitric acid being removed by passing a current of dry air over the crystals heated in a tube at 60–80°.[3]

Chromium trioxide may also be obtained by the action of an excess of nitric acid of density 1·38 on barium chromate, the barium nitrate being separated by crystallisation.[4]

Chromium trioxide exists either as a red, woolly mass or as lustrous, scarlet, rhombic prisms; it has a density of 2·78, and melts[5] at 198° to a dark red liquid, which solidifies to a reddish-black, crystalline mass, having a metallic appearance. At about 420° it is completely resolved into oxygen and the sesquioxide.[6]

Chromium trioxide is easily converted into chromic oxide by reducing agents, such as sulphur dioxide, hydrogen sulphide, stannous chloride, arsenious oxide, ferrous salts, zinc, etc., and many organic compounds also act in the same way. Thus if strong alcohol be dropped on to the dry trioxide reduction takes place with incandescence; paper, sugar, oxalic acid, etc., also reduce the solution of the trioxide, especially on warming. When the trioxide is heated with aqueous hydrochloric acid, chlorine is liberated, the dry gas yielding chromyl chloride (p. 1070), and when heated with sulphuric acid it decomposes with evolution of oxygen. The aqueous solution of chromium trioxide as well as its solution in glacial acetic acid is often used in organic chemistry as an oxidising agent. Still more commonly, a mixture of potassium dichromate and dilute sulphuric acid is employed for this purpose, in which case chrome alum is obtained as a by-product. Chromium trioxide dissolves without alteration in cold dilute alcohol and pure ether, and it is soluble also in concentrated sulphuric acid, apparently[1] with formation of the compounds CrO_3,SO_3 and CrO_3,SO_3,H_2O, but least in acid containing 16–17 per cent. of water. It deliquesces in the air, forming a brown solution which on dilution with water becomes yellowish-red. This dyes the skin, as well as silk and wool, a yellow colour, and possesses an acid and astringent taste.

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[1] Askenasy and Révai, *Zeit. Elektrochem.*, 1913, **19**, 344; Boehringer, Ger. Pat., 261694; *Zeit. Elektrochem.*, 1913, **19**, 248; Goldberg, Ger. Pat., 303165.

[2] *Pogg. Ann.*, 1871, **143**, 471.

[3] Bunsen, *Annalen*, 1868, **148**, 290.

[4] Duvillier, *Compt. rend.*, 1872, **75**, 711.

[5] Jaeger and Germs, *Zeit. anorg. Chem.*, 1921, **119**, 145.

[6] Honda and Soné, *Sci. Rep. Tôhoku Imp. Univ.*, 1914, **3**, 223.

Chromic Acid, H_2CrO_4.—The existence in the solid condition of normal chromic acid has been asserted by Moissan.[2] From the conductivity, molecular refractivity, and molecular solution volume it has been concluded[3] that solutions of chromium trioxide contain only dichromic acid, $H_2Cr_2O_7$; on the other hand, Costa[4] and Dehn[5] consider that both chromic and dichromic acids are present in a state of equilibrium. It is observed that in very dilute solutions, chromic acid, dichromates, and chromates have identical colour; the hydrolysis $H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$ is then regarded as complete; more concentrated solutions contain both chromic and dichromic acids, whereas further increase of concentration or temperature apparently dehydrates the molecules, forming *trichromic acid*, $H_2Cr_3O_{10}$, and *tetrachromic acid*, $H_2Cr_4O_{13}$, the salts of which may be represented as $(M'O)CrO_2{\cdot}O{\cdot}CrO_2{\cdot}O{\cdot}CrO_2(OM')$ and

$$(M'O)CrO_2{\cdot}O{\cdot}CrO_2{\cdot}O{\cdot}CrO_2{\cdot}O{\cdot}CrO_2(OM')$$

respectively.

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[1] Gilbert, Buckley and Masson, *J. Chem. Soc.*, 1922, 121, 1934; Meyer and Stateczny, *Zeit. anorg. Chem.*, 1922, 122, 1.

[2] Moissan, *Compt. rend.*, 1884, 98, 1581.

[3] Ostwald, *Zeit. physikal. Chem.*, 1888, 2, 78; Datta and Dhar, *J. Amer. Chem. Soc.*, 1916, 38, 1303.

[4] Costa, *Gazz.*, 1906, 36, i., 535.

[5] Dehn, *J. Amer. Chem. Soc.*, 1914, 36, 829; Dhar, *Zeit. anorg. Chem.*, 1921, 121, 99.

Chromic acid, $CrO_2(OH)_2$, in its chemical properties resembles sulphuric acid, and the normal salts are usually isomorphous with the corresponding sulphates; similarly, dichromic acid corresponds to disulphuric (pyrosulphuric) acid.

By direct solution of metals[1] or by reaction with bases, there are produced the normal chromates and dichromates, of which potassium dichromate is the most important.

Normal Potassium Chromate, K_2CrO_4, is obtained by the addition of potassium hydroxide to a solution of the dichromate, evaporation yielding yellow, rhombic pyramids which are isomorphous with potassium sulphate. Potassium chromate has a density of 2·71 at 3·9°, and does not undergo alteration in the air. On heating to 666° it is converted into a second modification; it becomes red-coloured, and melts at 978° without decomposition, solidifying on cooling to a crystalline mass. It dissolves in water with a yellow colour which is perceptible even when very small quantities of the substance are present, one part of the salt imparting a distinct yellow tint to 400,000 parts of water. One hundred parts of water dissolve[2] at

−11·4°*	0°	30°	60°	105·6°†
54·57	57·11	65·13	74·60	88·8 parts.

* Cryohydric point. † Boiling point of saturated solution.

The salt has a bitter, cooling taste and an alkaline reaction. On evaporating its solution, red crystals of the dichromate are first deposited and afterwards the yellow crystals of the normal salt. It is decomposed by all acids, even by carbonic acid, with formation of the dichromate. It is insoluble in alcohol.

Potassium Dichromate, or *Bichromate of Potash*, $K_2Cr_2O_7$, serves as the starting point for the preparation of almost all the other chromium compounds, and is prepared on the large scale from chrome iron ore.

Up to the year 1820 potassium dichromate was used only for the purpose of making chrome yellow, and was prepared by the calcination of chrome iron ore with costly saltpetre. In the above year Köchlin introduced potassium dichromate into the process of Turkey-red dyeing, and it was soon employed for a variety of other purposes, especially in wool dyeing. In its preparation, potashes were employed instead of saltpetre, and the chrome iron stone was oxidised in reverberatory furnaces by means of atmospheric oxygen. An important improvement was made in the process by Stromeyer by the introduction of a certain quantity of lime together with the potash. Not only was a saving of alkali thus effected, but the oxidation was rendered easier, inasmuch as the whole mass did not fuse, and therefore remained porous and more capable of absorbing the atmospheric oxygen. The chrome iron ore is first roasted and 4½ parts of the finely ground ore are mixed with 2½ parts of potassium carbonate and 7 parts of lime. This mass after drying at 150° is heated to bright redness with an oxidising flame, the whole being constantly stirred. At the end of the operation the charge is withdrawn from the furnace, and, after cooling, is lixiviated with the minimum amount of hot water. If calcium chromate be found in solution, a hot saturated solution of potassium sulphate is added, when the calcium is thrown down as sulphate and potassium chromate remains in solution. The liquor is next treated with the requisite quantity of sulphuric acid, diluted with twice its volume of water, to convert the chromate into dichromate, and allowed to cool. The solution of chromate saturated at 16° contains nearly 1 part of salt to 2 parts of water, whilst the dichromate requires 10 parts of water for its solution; hence when the saturated solution of chromate is converted into dichromate, a precipitate of about 75 per cent. of the dichromate is formed on cooling. The precipitate is collected and recrystallised. The mother-liquor, which contains potassium sulphate, is used to lixiviate another portion of the roasted mass.

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[1] See van Name and Hill, *Amer. J. Sci.*, 1916, [4], **42**, 301; 1918, [4], **45**, 54.

[2] Koppel and Blumenthal, *Zeit. anorg. Chem.*, 1907, **53**, 262.

An important modification of this procedure consists in the manufacture of sodium dichromate (p. 1065) by a similar process, and the final conversion of this into the potassium salt.

This salt may be produced also by electrolysing a solution of potassium hydroxide or a potassium salt, using an anode of ferrochrome.[1]

Potassium dichromate crystallises in splendid garnet-red tablets or prisms belonging to the triclinic system, having a density of 2·692 at 3·9°. It melts at 396°, forming a transparent, red liquid, which when slowly cooled crystallises in the same form as from aqueous solution. It is unchanged in the air, and decomposes at a white heat into oxygen, chromic oxide, and the normal salt. One hundred parts of water dissolve[1] at

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[1] Lorenz, *Zeit. anorg. Chem.*, 1896, 12, 396; C. F. Griesheim-Elektron, Ger. Pat., 143320.

−0·63° *	0°	30°	60°	104·8° †
4·50	4·64	18·09	46·10	106·2 parts of salt.

* Cryohydric point. † Boiling point of saturated solution.

Potassium dichromate has an acid reaction, a cooling, bitter, metallic taste, and is insoluble in alcohol; it acts as a powerful poison, probably on account of its oxidising properties. The commercial salt is usually almost chemically pure, and is employed for the preparation of other chromium compounds, as a reagent, and as an oxidising agent, as well as being largely used in dyeing and calico-printing.

A film of organic matter saturated with a solution of potassium dichromate acquires a dark colour on exposure to light owing to a reduction to chromic oxide taking place, and a solution in gelatin is used as a sensitive agent in the Autotype and other similar photographic printing processes, commonly referred to as "carbon printing." These processes depend not merely upon the de-oxidation of the dichromate, but also upon the fact that this reduction renders the gelatin insoluble in, and non-absorbent of, water, so that those portions of the gelatin film which have been acted upon by the light remain unchanged when the film is immersed in hot water, whilst those parts which have been protected from the action of the light dissolve away entirely. A film is thus obtained in which the various shades of the original negative are represented by deposits of varying thickness of the insoluble gelatin, which can be coloured with a wide range of pigments; in this way the red or blue chalk drawings of the old masters can be reproduced with remarkable accuracy.[2]

Potassium dichromate forms a double salt with mercuric chloride, $K_2Cr_2O_7,HgCl_2$, which separates in red, well-developed, rhombic crystals.

Potassium Trichromate, $K_2Cr_3O_{10}$, is formed by the action of chromic acid solution on the dichromate, but is best prepared by boiling the dichromate with nitric acid of density 1·19; on cooling, potassium nitrate separates almost completely, and the decanted liquor then deposits the trichromate in deep red, monoclinic prisms of density 2·648. It is decomposed by hot water into chromic acid and the dichromate, and cannot therefore be recrystallised in this manner.[1]

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[1] Koppel and Blumenthal, *Zeit. anorg. Chem.*, 1907, 53, 262.

[2] For a full and interesting description of these processes, see Abney's *Treatise on Photography*. (Longmans.)

Potassium Tetrachromate, $K_2Cr_4O_{13}$, is obtained by heating the dichromate with nitric acid of density 1·41, and separates out on cooling in brownish-red crusts consisting of small, rhombic plates. It has a density of 2·649, and, like the trichromate, is decomposed by water into chromic acid and the dichromate.

Normal Sodium Chromate, $Na_2CrO_4,10H_2O$, is obtained by direct oxidation of chromite in presence of lime and soda (p. 1059), by fusing chromic oxide and sodium nitrate together, and evaporating the solution at a low temperature, or by allowing a solution of potassium chromate saturated with soda to evaporate at 0°. However, the only method of obtaining the pure salt is by addition of sodium carbonate to a solution of carefully purified sodium dichromate. The salt is deposited in deliquescent, transparent, yellow prisms, isomorphous with Glauber's salt. When the solution is heated to above 65° the anhydrous salt separates out. It has an alkaline reaction, and a bitter, metallic taste. Hydrates containing $4H_2O$ and $6H_2O$ have also been obtained.[2]

Sodium Dichromate, $Na_2Cr_2O_7,2H_2O$ crystallises in thin, triclinic, yellowish-red, deliquescent prisms. This salt is now manufactured on a large scale, since for many technical purposes it can replace the more expensive potassium salt. It is much more soluble than the latter, and for this reason is used as a depolariser in chromic acid cells in place of the potassium salt. Above 83°, aqueous solutions deposit the anhydrous salt, a deliquescent substance which melts at 230° and decomposes at 400°.

The following salts are also known: *sodium trichromate*, $Na_2Cr_3O_{10},H_2O$, *sodium tetrachromate*, $Na_2Cr_4O_{13},4H_2O$, and a *basic chromate*, $Na_4CrO_5,13H_2O$.

Ammonium Chromate, $(NH_4)_2CrO_4$.—This salt can be obtained pure only from solutions containing excess of ammonia, as it readily loses the latter, forming the dichromate. It is obtained in golden-yellow, monoclinic needles by gently warming pure chromium trioxide with a quantity of ammonia just sufficient to dissolve the chromate formed, and cooling the solution in a freezing mixture. One hundred parts of water at 30° dissolve 40·46 parts of the salt. The *dichromate*, $(NH_4)_2Cr_2O_7$, is readily obtained by adding the requisite quantity of chromium trioxide to ammonia, and separates out on evaporation in orange-red, monoclinic crystals of density 2·367. At 30°, 47·17 parts dissolve in 100 parts of water. The substance is stable in air, even at 100°, but on ignition it decomposes into nitrogen, water, a bulky, leaf-like mass of chromium sesquioxide, and generally a little ammonia. This salt forms a number of crystalline double salts with mercuric chloride.[1]

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[1] Jäger and Krüss, *Ber.*, 1889, **22**, 2038.

[2] Salkowski, *Ber.*, 1901, **34**, 1947; Richards and Kelley, *J. Amer. Chem. Soc.*, 1911, **33**, 847.

The *trichromate* and *tetrachromate* have also been prepared.

Chromates, dichromates, etc., of the other alkali metals are known, as well as a number of double salts; these are formed not only amongst the alkali chromates themselves, and between the alkali chromates and chromates of other metals, but also between the alkali chromates and mercuric chloride and cyanide.

474 Most of the other metals form chromates or basic chromates which are for the most part coloured substances insoluble in water, many of which are largely used as pigments. The most important of these are the following:

Copper Chromates.—Copper Dichromate, $CuCr_2O_7,2H_2O$, is obtained by the action of concentrated chromic acid solution on copper hydroxide. It forms blackish-brown, deliquescent crystals. The solution when boiled deposits the basic salt $Cu_3CrO_6,2H_2O$[2] as a brown precipitate, which is also obtained when boiling solutions of normal potassium chromate and copper sulphate are mixed; cold solutions, on the other hand, yield a double salt. The mineral vauquelinite, $(Cu,Pb)_3Cr_2O_9$, occurs in small, glistening, monoclinic crystals or earthy masses, together with crocoisite. *Normal copper chromate*, $CuCrO_4$, forms mixed crystals with copper sulphate.

Silver Chromate, Ag_2CrO_4, is obtained as a brick-red, amorphous precipitate when a solution of potassium chromate is poured into excess of a concentrated solution of silver nitrate either cold or hot.[3] It is formed when silver dichromate is boiled for a long time with water as a deep green, crystalline powder,[4] which is insoluble in water, but dissolves with some difficulty in sulphuric acid, nitric acid, or ammonia. The solution obtained by dissolving silver chromate in as small a quantity as possible of warm ammonia of density 0·94 deposits ammonio-silver chromate, $Ag_2CrO_4,4NH_3$, on cooling in long, yellow needles[1] which by heating yield green silver chromate.

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[1] Jäger and Krüss, *Ber.*, 1889, **22**, 2047.

[2] Gröger, *Monatsh.*, 1903, **24**, 483.

[3] Autenrieth, *Ber.*, 1902, **35**, 2067.

[4] Margosches, *Zeit. anorg. Chem.*, 1904, **41**, 68; 1906, **51**, 231; Köhler, *ibid.*, 1916, **96**, 207.

The red chromate may be converted into the green form by heating in an atmosphere of carbon dioxide (Autenrieth).

Silver Dichromate, $Ag_2Cr_2O_7$, is obtained by the action of potassium dichromate on silver nitrate in acid solution; it forms small, red, triclinic crystals, and is decomposed by boiling water into chromic acid and normal chromate. It is also obtained by warming silver chromate with dilute nitric acid.[2]

Barium Chromate, $BaCrO_4$, is a yellow precipitate, insoluble in acetic, but easily souble in nitric, hydrochloric, and aqueous chromic acids. From the last solvent, the salt $BaCr_2O_7,2H_2O$ may be obtained in yellow, stellar needles, which are decomposed by water with separation of the normal salt. Barium chromate is used as a pigment under the name of *yellow ultramarine* or *lemon chrome*. It is, however, now very little used, as the lead chromates have a brighter colour and more body.

Zinc Chromates.—Potassium chromate gives with zinc sulphate a yellow precipitate of basic zinc chromate, $Zn_2(OH)_2CrO_4,H_2O$. A similar compound, $2Zn_2(OH)_2CrO_4,H_2O$, is formed when zinc carbonate is heated with a solution of chromic acid. The normal chromate and dichromate have also been prepared.

If a salt or oxide of zinc is boiled with potassium dichromate the yellow compound, $Zn_4(OH)_6CrO_4$, is precipitated.

The chromate obtained by the addition of a hot neutral solution of zinc sulphate to potassium chromate forms a stable yellow pigment sold under the name of *Zinc yellow* or *Buttercup yellow*.

Lead Chromate, $PbCrO_4$, occurs as crocoisite in translucent, yellow, monoclinic prisms, having a density of 5·9 to 6·1. The mineral is found in Siberia, in the Urals, Brazil, Hungary, and the Philippine Islands. Crystals of somewhat higher density are artificially obtained when lead chloride is strongly heated with potassium chromate, as well as when solutions of lead acetate and normal potassium chromate are allowed slowly to diffuse into one another.[3] A bright yellow precipitate of the normal chromate is obtained when a solution of a lead salt is precipitated with potassium dichromate. The reaction $PbSO_4 + K_2CrO_4 = PbCrO_4 + K_2SO_4$ is practically complete, and can be used[1] for the manufacture of the normal salt, which is known as *chrome yellow*, *Paris yellow*, or *Leipsig yellow*, and is largely used as a pigment. It is insoluble in water, but is readily dissolved by nitric acid and potassium hydroxide solution. When strongly heated it fuses to a brown liquid, which on cooling solidifies to a crystalline mass.[2] Since lead chromate at a red heat oxidises all organic substances, it is frequently employed in organic analysis, especially in the case of bodies which contain chlorine, sulphur, etc. The chrome yellow of commerce often contains admixtures, especially lead sulphate. This, however, is not always to be considered as an adulteration, and it is used for the preparation of a light shade. This is termed *Cologne yellow*, and is obtained by the precipitation of a mixture of the nitrates of lead and calcium with a mixture of sodium sulphate and potassium chromate, or more generally by heating lead sulphate with a solution of potassium dichromate.

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[1] Muthmann, *Ber.*, 1889, **22**, 2051.

[2] Autenrieth, *Ber.*, 1902, **35**, 2059; Sherrill, *J. Amer. Chem. Soc.*, 1907, **29**, 1641; Spitalsky, *Chem. Zentr.*, 1914, ii, 376.

[3] Drevermann, *Annalen*, 1853, **87**, 121.

Calico is printed or dyed with chrome yellow by first mordanting the cloth with a solution of a lead salt, and afterwards steeping it in one of a soluble chromate.

Basic Lead Chromate, Pb_2CrO_5, is known in commerce as *chrome red* and is obtained as a fine red powder by digesting chrome yellow with cold sodium hydroxide solution, boiling it with a solution of normal potassium chromate, or fusing it with potassium nitrate. Another basic salt, $Pb_3Cr_2O_9$, occurs as the mineral phœnicite, in hyacinth-red crystals of density 5·75; the salt $4PbO,CrO_3,H_2O$ is known, as also[3] are Pb_5CrO_8 and $Pb_7Cr_2O_{13}$.

By making a suitable mixture of chrome yellow and chrome red, or by modifying the process of manufacture so as to obtain a mixture of these, pigments of any shade between the two may be obtained. These are known commercially as *chrome orange.*

Lead dichromate and the chromate and dichromate of quadrivalent lead have been prepared by an electrolytic method.[4]

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[1] Milbauer and Kohn, *Zeit. physikal. Chem.*, 1910, **91**, 410.

[2] Jaeger and Germs, *Zeit. anorg. Chem.*, 1921, **119**, 145, find that lead chromate is trimorphous; the α-form is stable below 707°, the β-form between 707° and 783°, and the γ-form above 783°, melting at about 844° with evolution of oxygen.

[3] Jaeger and Germs, *loc. cit.*

[4] Elbs and Nübling, *Zeit. Elektrochem.*, 1903, **9**, 776. See also Mayer, *Ber.*, 1903, **36**, 1740; Cox, *Zeit. anorg. Chem.*, 1906, **50**, 226.

Bismuth Chromate.—Normal *bismuth chromate* is unknown, but a number of basic salts have been described. By addition of potassium chromate solution to a solution of bismuth nitrate, the compound $K_2O,Bi_2O_3,4CrO_3$ is obtained as a yellow precipitate; on boiling this with water, the compound $Bi_2O_3,2CrO_3$ or *bismuthyl dichromate*, $(BiO)_2Cr_2O_7$, is obtained as orange-yellow crystals, insoluble in water.

Chromic Chromate, $Cr_2O_3,CrO_3 = 3CrO_2$.—This compound, also known as *chromium dioxide,* is formed when chromic nitrate is gently heated, or when a solution of chromic oxide in nitric acid is evaporated to remove excess of acid and the residue dissolved in water and treated with ammonium hydroxide.[1] It is likewise prepared by the partial reduction of the trioxide, and by the precipitation of a chromic salt with a soluble chromate. The brown powder thus obtained is easily soluble in acids. Alkalis precipitate chromic hydroxide from its solution, whilst a chromate remains in the liquid. If chromic chromate be washed for some time with water, it is decomposed into soluble trioxide and insoluble sesquioxide; for these reasons the substance is regarded as a chromate. When nitric oxide is passed into a tolerably concentrated solution of potassium dichromate, chromic chromate is obtained as a dark brown precipitate, which dries at 250° to form a black, hygroscopic powder, and this, when heated in a current of hydrogen chloride, yields chromic oxide, water, and chlorine.

A hygroscopic black powder has also been obtained by Manchot and Kraus[2] by heating chromic hydroxide in a current of oxygen. This contains a little water, which it gives off at a red heat along with some of its oxygen; chromic oxide remains. When washed with water, no chromium trioxide is obtained, and these investigators therefore consider it to be a dioxide, CrO_2, and not chromic chromate.

When the vapour of chromyl chloride is passed through a red hot tube, violet, translucent prisms, having the composition Cr_5O_9 (*i.e.*, $2Cr_2O_3,CrO_3$), are obtained. These are magnetic, and on ignition are gradually converted into chromic oxide.[3]

An oxide of the formula Cr_4O_9 (*i.e.*, $Cr_2O_3,2CrO_3$) has been described as being the product of the ignition of the trioxide between 500° and 510°.[1]

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[1] Jovitschitsch, *Helv. Chim. Acta*, 1920, **3**, 40. See also Hooton, *Proc. Chem. Soc.*, 1908, **24**, 27; Ogata, *J. Pharm. Chim.*, 1916, [7], **14**, 144.

[2] *Ber.*, 1906, **39**, 1352. See also Meerburg, *Zeit. anorg. Chem.*, 1907, **54**, 31.

[3] Geuther, *Annalen*, 1861, **118**, 61; Soné and Ishiwara, *Sci. Rep. Tôhoku Imp. Univ.*, 1914, **3**, 271.

A number of crystalline double chromates have been described which have the general formula $M'_2M''(CrO_4)_2,6H_2O$, where M' is K, Rb, NH_4, or Cs, and M'' is Ni, Mg, or Cd, as well as ammoniacal double chromates of the formula $M'_2M''(CrO_4)_2,2NH_3$, where M' is K or NH_4, and M'' is Cu, Zn, Cd, Ni, or Co.[2]

HALOGEN AND AMIDO-DERIVATIVES OF CHROMIC ACID.

475 *Chromyl Difluoride*, CrO_2F_2.—This substance was first obtained by Unverdorben by the action of sulphuric acid on a mixture of lead chromate and fluorspar, and was regarded by him as chromium hexafluoride; Oliveri[3] has, however, characterised it as chromyl fluoride, derived from chromic acid by the replacement of the two hydroxyl groups by fluorine. Ruff's[4] attempt to obtain a substance of definite composition by this method, or, better, by substituting fluorosulphonic acid for calcium fluoride and sulphuric acid, and a mixture of potassium dichromate and chromium trioxide for potassium dichromate alone, was, however, unsuccessful. The substance is obtained as a red gas, condensing in a freezing mixture to a very volatile, blood-red liquid which attacks glass, and is converted by the moisture of the air into chromium trioxide and hydrogen fluoride.

Fluorochromic acid, $CrO_2F(OH)$, is unknown in the free state, but its *potassium* salt is formed by heating potassium dichromate with hydrofluoric acid in a platinum vessel; it crystallises in red, tetragonal pyramids, which are soluble in water, but the solution decomposes on boiling into potassium dichromate and hydrofluoric acid. The *ammonium* salt is also known.

Chromyl Dichloride, CrO_2Cl_2, appears to have been discovered by Thomson[5]; it was also investigated by Berzelius,[6] Dumas,[7] and Wöhler.[8] It is prepared[9] by treating a dry, finely divided mixture of five parts of common salt and eight parts of potassium dichromate with fifteen parts of fuming sulphuric acid added in small quantities, and finally gently warming the mixture; in order to remove free chlorine, the distillate is repeatedly rectified in a current of carbon dioxide. It is also formed by heating chromium trioxide in a current of hydrogen chloride, when it distils over, and an oily liquid remains which has been thought to be *chlorochromic acid*, Cl·CrO$_2$·OH. It may readily be obtained by dissolving chromic acid in concentrated hydrochloric acid, and adding sulphuric acid to the cooled liquid in small quantities at a time. The heavier chromyl chloride is then run off, dry air is blown through, and the liquid distilled.[1] It may also be obtained[2] in 80 per cent. yield by addition of acetyl chloride to a solution of chromium trioxide in carbon tetrachloride. Chromyl dichloride is a mobile liquid of a splendid blood-red colour by transmitted, and nearly black by reflected light. It boils at 116·7°, and has a density at 25° of 1·912.[3] The molecular weight of chromyl chloride, determined by the usual methods, gives values corresponding to the above formula. It absorbs chlorine readily, dissolves iodine, and when dropped into water it remains unaltered for a few seconds, but is afterwards decomposed with violent ebullition into chromic and hydrochloric acids. When brought into contact with phosphorus it explodes, whilst it takes fire in contact with sulphur, hydrogen sulphide, ammonia, alcohol, and many other organic bodies, and when diluted with acetic acid or carbon tetrachloride acts as an oxidising and chlorinating agent upon hydrocarbons. With phosphorus halides it yields additive compounds.[4] When chromyl dichloride is heated in a closed tube to 180° for three or four hours, *trichromyl chloride*, $Cr_3O_6Cl_2$, is formed as a black powder, which deliquesces on exposure to the air;[5] another solid oxychloride is stated to have the composition $(CrO_2)_5Cl_6$.[6]

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[1] Shukow, *Compt. rend.*, 1908, **146**, 1390.

[2] Briggs, *Journ. Chem. Soc.*, 1903, **83**, 1391; 1904, **85**, 672, 677.

[3] Oliveri, *Gazz.*, 880, **16**, 218.

[4] Ruff, *Ber.*, 1914, **47**, 656.

[5] *Phil. Trans.*, 1827, **117**, 159.

[6] *Berz. Jahresber.*, 1827, **6**, 129.

[7] *Ann. Chim. Phys.*, 1826, [2], **31**, 453; Walter, *ibid.*, 1837, [2], **66**, 387.

[8] *Pogg. Ann.*, 1834, **33**, 343.

[9] Moles and Gomez, *Zeit. physikal. Chem.*, 1912, **80**, 513; *Anal. Fís. Quím.*, 1914, **12**, 142.

Bromine and iodine do not form analogous chromyl derivatives; a bromide or iodide, heated with sulphuric acid and potassium dichromate, yields free bromine or iodine. This reaction is made use of for the detection of chlorine in presence of bromine or iodine; if chlorine be present the substance, when heated with potassium dichromate and sulphuric acid, yields chromyl chloride, which is converted by water into chromic acid, which may be recognised by the usual tests.

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[1] Law and Perkin, *Journ. Chem. Soc.*, 1907, **91**, 191.

[2] Fry, *J. Amer. Chem. Soc.*, 1911, **33**, 697.

[3] Moles and Gomez, *loc. cit.* See also Thorpe, *Journ. Chem. Soc.*, 1880, **37**, 327.

[4] Fry and Donnelly, *J. Amer. Chem. Soc.*, 1916, **38**, 1923; 1918, **40**, 478.

[5] Thorpe, *Journ. Chem. Soc.*, 1870, **23**, 31.

[6] Pascal, *Compt. rend.*, 1909, **148**, 1463.

Chlorochromic acid, $Cl{\cdot}CrO_2{\cdot}OH$, analogous to chlorosulphonic acid, is unknown, but its *potassium* salt is formed[1] when three parts of potassium dichromate are gently heated with four parts of concentrated hydrochloric acid and a small quantity of water, or when chromyl dichloride is added to a saturated solution of potassium chloride:

$$CrO_2Cl_2 + KCl + H_2O = KCrO_3Cl + 2HCl.$$

It crystallises in flat, red, rectangular prisms, having a density of 2·497. The salt is partially decomposed by water, but may be recrystallised from water containing hydrochloric acid, or from glacial acetic acid. It decomposes at 100° with evolution of chlorine:

$$4CrO_2(OK)Cl = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2$$

Other chlorochromates have been described,[2] as well as potassium bromo- and iodo-chromates.

Amidochromic acid, $NH_2{\cdot}CrO_2{\cdot}OH$.—It is doubtful whether, by the action of dry ammonia on chlorochromates in solution or suspension in organic media, salts of amidochromic acid are formed, as has been suggested;[3] liquid ammonia, however, apparently leads to the formation of salts of *imidochromic acid*, $NH{:}CrO(OH)_2$.[4]

Perchromic Acid and the Perchromates.—A deep indigo-blue coloured solution is obtained when hydrogen peroxide is added to an aqueous solution of chromium trioxide, or to a solution of a chromate acidified with sulphuric acid. If the freshly prepared solution be shaken with ether, this liquid takes up the perchromic acid and becomes of a dark blue colour. The ethereal solution is more stable than the aqueous solution, but on evaporation it leaves a residue of chromium trioxide. The same decomposition is effected by alkalis, a chromate being formed with evolution of oxygen. The colouring power of perchromic acid is so great that its formation is employed as a most delicate test, both for chromic acid and for hydrogen peroxide. The deepest coloration is produced when two molecules of hydrogen peroxide are used to one molecule of chromium trioxide. The constitution of the substance thus formed is as yet uncertain. It has been variously regarded as Cr_2O_7,xH_2O,[1] $CrO_4,3H_2O$,[2] CrO_3,H_2O_2,[3] and $2HCrO_4,H_2O_2$,[4] etc. By the action of sodium peroxide on a thin paste of chromic hydroxide and water Häussermann[5] obtained a sodium salt having the composition $Na_6Cr_2O_{16},28H_2O$, which would be the salt of an acid derived from the anhydride CrO_6. When this salt is treated with sulphuric acid, the characteristic blue colour is first produced, but oxygen is soon evolved, and chromic sulphate remains in solution. Salts of a perchromic acid, $HCrO_5$, [$O_3Cr{\cdot}O{\cdot}(OH)$, in which chromium is septavalent], with pyridine, quinoline, and other organic bases have been prepared by Wiede,[6] by adding the bases to the blue ethereal solution of perchromic acid cooled below 0°. These are explosive crystalline compounds, which evolve oxygen when treated with strong acids. In a similar manner, he has obtained blue potassium and ammonium salts, which he regards as $(NH_4)CrO_5,H_2O_2$ and $KCrO_5,H_2O_2$, the hydrogen peroxide acting like water of crystallisation. On the other hand, according to Riesenfeld,[7] the last two compounds are acid salts of the perchromic acid, H_3CrO_7, and have, therefore, formulæ of the type $R^IH_2CrO_7$. They are also formed by the action of hydrogen peroxide on chromates in cold, faintly acid solution; in alkaline solution red salts of a perchromic acid, H_3CrO_8, are obtained. The red ammonium salt, $(NH_4)_3CrO_8$, with dilute acids, gives off oxygen and forms the blue salt, $(NH_4)H_2CrO_7$, and both these compounds yield with pyridine Wiede's salt of the acid $HCrO_5$; finally, all three compounds with excess of ammonia form triammine chromium tetroxide, $CrO_4,3NH_3$. This compound[8] is a brown, explosive, crystalline substance which has density 1·964 at 15·8°.

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[1] Péligot, *J. Pharm.*, 1833, **19**, 301.

[2] Péligot, *Ann. Chim. Phys.*, 1833, [2], **52**, 267; Praetorius, *Annalen*, 1880, **201**, 1; Loewenthal, *Zeit. anorg. Chem.*, 1894, **6**, 355.

[3] Heintze, *J. pr. Chem.*, 1871, [2], **4**, 212; Loewenthal, *loc. cit.*; Wyrouboff, *Bull. Soc. chim.*, 1894, [3], **11**, 845; Werner and Klein, *Zeit. anorg. Chem.*, 1895, **9**, 291; Meyer and Best, *ibid.*, 1900, **22**, 192.

[4] Rosenheim and Jacobsohn, *Zeit. anorg. Chem.*, 1906, **50**, 297.

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[1] Barreswil, *Ann. Chim. Phys.*, 1847, [3], **20**, 364.

[2] Fairley, *Chem. News*, 1876, **33**, 337.

[3] Moissan, *Compt. rend.*, 1883, **97**, 96.

[4] Berthelot, *ibid.*, 1889, **108**, 25.

[5] *J. pr. Chem.*, 1893, [2], **48**, 70.

[6] *Ber.*, 1897, **30**, 2178; 1898, **31**, 516, 3139; 1899, **32**, 378. See also Hofmann and Hiendlmaier, *ibid.*, 1905, **38**, 3059.

[7] *Ber.*, 1905, **38**, 4066; 1908, **41**, 2826; 1911, **44**, 147; *Zeit. anorg. Chem.*, 1912, **74**, 46. Compare Hofmann and Hiendlmaier, *Ber.*, 1904, **37**, 1663.

[8] Wiede, *Ber.*, 1897, **30**, 2178; 1899, **32**, 378; Riesenfeld, Wohlers, Kutsch, and Ohl, *Ber.*, 1905, **38**, 1885, 3380.

Riesenfeld considers that when excess of hydrogen peroxide acts on a solution of chromic acid, the acid H_3CrO_8 (which, though blue, has a composition corresponding to the red perchromates) is mainly produced, but at the same time a little of the acid H_3CrO_7 is also formed, whilst the blue ethereal solution probably contains a mixture of several perchromic acids.[1] When perchromic acid is prepared by the action of hydrogen peroxide on chromyl chloride or upon chromium trioxide in methyl ether solution at −30°, it is found to possess the formula $H_3CrO_8,2H_2O$; the water is water of constitution. Thus the blue acid may be regarded[2] as having the formula $(OH)_4Cr(O{\cdot}OH)_3$, whereas the red perchromates are anhydro-salts of the formula $(MO{\cdot}O)_3CrO_2$.

CHROMOUS SALTS.

476 By dissolving metallic chromium in acids, or by reduction of chromic salts or chromates with metals or by an electrolytic process,[3] compounds of bivalent chromium are obtained. It is essential that air should be excluded during the operation, since the chromous salts in solution are readily oxidised to chromic salts and chromic acid, with intermediate formation of unstable compounds.[4] They are powerful reducing agents.[5] The anhydrous salts are usually white, and yield solutions the colour of which is blue in the case of salts of strong acids, and yellow, brown, or red in other cases.

Chromous Fluoride, CrF_2, known only in the anhydrous condition, is a green, lustrous substance. It is obtained by the interaction of chromium or chromous chloride with hydrogen fluoride.

Chromous Chloride, $CrCl_2$, is formed by the ignition of chromium in hydrogen chloride, or of chromic chloride in a current of hydrogen gas free from oxygen, and forms white, silky, lustrous needles which are stable in dry air. It dissolves in water with evolution of heat, forming a blue solution, which absorbs oxygen with extreme avidity, yielding basic chromic salts, and forms a powerful reducing agent. The solution is sometimes employed in gas analysis for the absorption of oxygen. It is found, however,[1] that chromous chloride prepared by treating chromous acetate with hydrochloric acid is less stable than that prepared by reduction of chromic chloride in solution with nascent hydrogen; the latter solutions, however, do not give complete absorption. Further, acid solutions of chromous chloride spontaneously decompose with liberation of hydrogen:[2] $2CrO + H_2O = Cr_2O_3 + H_2$. Recoura[3] states that the solution may be obtained by adding a mixture of 300 c.c. of pure fuming hydrochloric acid with 200 c.c. of water to 300–400 grams of amalgamated granulated zinc and 50 grams of finely powdered potassium dichromate in a flask of about 3 litres capacity. A violent action occurs, the liquid becoming first green, then sky-blue.

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[1] See also Spitalsky, *Zeit. anorg. Chem.*, 1907, **53**, 184; 1907, **54**, 265; 1907, **56**, 72; 1910, **66**, 179; *Ber.*, 1910, **43**, 3187.

[2] Riesenfeld and Mau, *Ber.*, 1914, **47**, 548.

[3] Traube and Goodson, *Ber.*, 1916, **49**, 1679; Taylor, Gersdorff and Tovrea, *J. Amer. Chem. Soc.*, 1922, **44**, 612.

[4] Piccard, *Ber.*, 1913, **46**, 2477; Traube and Passarge, *Ber.*, 1913, **46**, 1505, have found that double salts with hydrazine are much more stable.

[5] Traube and Passarge, *Ber.*, 1916, **49**, 1692.

Hydrates of chromous chloride are known as follows: $6H_2O$, $4H_2O$ (dark blue), $4H_2O$ (dark green),[4] $3H_2O$, and $2H_2O$. With ammonia, white chromous chloride forms a violet triammine and an ashy-grey hexammine.[5]

The vapour density of chromous chloride at 1300° was found by Nilson and Pettersson to be 7·8, considerably lower than is required by the formula Cr_2Cl_4. At 1600° the density is further reduced to 6·2, showing that probably at a higher temperature its density would finally reach 4·25, corresponding to $CrCl_2$.[6]

Chromous Bromide, $CrBr_2$, is obtained by gently heating chromic bromide in hydrogen gas, and also by heating the metal in gaseous hydrobromic acid. It is a white, crystalline mass, yielding a green basic chromic bromide on exposure to moist air.

Chromous Iodide, CrI_2, is a crystalline mass obtained by heating chromium in gaseous hydriodic acid.[7]

Chromous Sulphide, CrS, is obtained by igniting chromous chloride in hydrogen sulphide, or by the long continued heating of chromic sulphide in hydrogen, and forms a black powder attacked only with difficulty by acids.[8] It may also be prepared by heating chromium to a high temperature in hydrogen sulphide, when it is obtained in needles having a density of 4·08, and sufficiently hard to scratch quartz.[1]

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[1] Anderson and Riffe, *J. Ind. Eng. Chem.*, 1916, **8**, 24.

[2] Traube and Passarge, *Ber.*, 1916, **49**, 1692.

[3] Recoura, *Compt. rend.*, 1887, **100**, 1227; *Ann. Chim. Phys.*, 1887, [6], **10**, 1.

[4] According to Werner's views, these isomeric tetrahydrates have the formulæ $[Cr(OH_2)_4]Cl_2$ and $[CrCl(OH_2)_3]Cl,H_2O$ respectively. See Knight and Rich, *J. Chem. Soc.*, 1911, **99**, 87.

[5] Ephraim and Millmann, *Ber.*, 1017, **50**, 529.

[6] *Journ. Chem. Soc.*, 1888, **53**, 830.

[7] Moissan, *Compt. rend.*, 1881, **92**, 1051.

[8] *Ibid.*, 1880, **90**, 817.

Chromous Sulphate, $CrSO_4,7H_2O$, is prepared by dissolving the metal in dilute sulphuric acid. It is best obtained by dissolving chromous acetate in dilute sulphuric acid; on cooling it separates in fine blue crystals isomorphous with ferrous sulphate. The ammoniacal solution absorbs oxygen, nitric oxide, and acetylene. If potassium sulphate be dissolved in a cold saturated solution of the chloride, alcohol added until a precipitate begins to form, and the mass kept for some weeks in absence of air, fine blue rhombic prisms, having the composition $K_2SO_4,CrSO_4,6H_2O$, and isomorphous with the corresponding ammonium salt, are deposited; these soon become green in the air owing to absorption of oxygen.

Chromous Carbonate, $CrCO_3$, is obtained by precipitating the chloride with potassium carbonate. A yellow to greenish-blue precipitate is obtained in the cold, which becomes reddish-brown on warming. Several double salts of chromous carbonate with the alkali carbonates have been prepared by the action of carbon dioxide on a mixture of solutions of chromous acetate and the alkali carbonate.[2] These are powerful reducing agents decomposing water at 100° with evolution of hydrogen.

Chromous Acetate is a red, crystalline precipitate obtained by addition of a concentrated solution of sodium acetate, saturated with carbon dioxide, to a solution of chromous chloride, and washing the product with air-free water.

CHROMIC SALTS.

477 The normal chromic salts have a blue or violet colour, and allow red light to pass through their solutions. The cold solutions have a violet colour, which on heating changes to green; in some cases the solution immediately becomes violet on cooling, but in others this occurs only on keeping the cooled solution for some time. Only the violet solutions of the salts with oxy-acids yield crystalline salts, the green solutions depositing an amorphous mass on evaporation. Many attempts have been made to explain the changes which take place, and much light has been thrown on the subject by the researches of Recoura

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[1] Mourlot, *Compt. rend.*, 1895, **121**, 943; Wedekind and Horst, *Ber.*, 1915, **48**, 105.

[2] Baugé, *Compt rend.*, 1896, **122**, 474; 1897, **125**, 1177; 1898, **126**, 1566.

and others. The salts which have been most closely examined are the chloride, bromide, and sulphate.

A certain complexity is thus introduced into the chemistry of the chromic salts owing to the existence of isomeric compounds the constitution of which can best be investigated from the point of view of Werner's[1] ideas of co-ordination compounds. Thus the chloride forms three distinct hexahydrates, and the bromide two distinct hexahydrates. These ionise differently in water, yielding solutions from which one-third, two-thirds, or the whole of the chlorine is precipitable by silver nitrate solution. The constitution of such isomers will be discussed later.

CHROMIUM AND THE HALOGENS.

478 *Chromic Fluoride*, CrF_3.—The anhydrous salt is obtained by passing hydrogen fluoride over heated chromic chloride, and sublimes at about 1200° in rhombohedra. Hydrates with 3·5, 6, and $9H_2O$ are known. The last named, $[Cr(H_2O)_6]F_3,3H_2O$, is obtained by adding ammonium fluoride to a cold solution of chromic sulphate. It is sparingly soluble in water, but dissolves in hydrochloric acid, forming a violet solution. When heated in the air it becomes green, and finally leaves a residue of chromium trioxide.[2] The salt is used to some extent in the dyeing of wool.

Double fluorides with other metallic fluorides are known, as well as various complex salts.[3] In the case of the salt of the composition $Cr_2F_2Cl_4$, the fluorine is not precipitable by barium chloride.[4]

Chromic Chloride, $CrCl_3$.—The anhydrous chloride is obtained[5] by heating metallic chromium or an intimate mixture of chromic oxide and carbon to dull redness in a stream of dry chlorine. It forms peach-blossom coloured scales, which have a density of 2·76. It volatilises at 1065°, yielding a vapour of the density 6·135, the formula $CrCl_3$ requiring 5·478, and Cr_2Cl_6 corresponding to a density twice as great; hence this latter compound cannot exist in the state of vapour. From 1190° up to 1300° the density is 5·5 (Nilson and Pettersson). Chromic chloride is almost insoluble in cold water, but it is readily soluble in presence of a very small quantity (less than 0·001 per cent.) of chromous chloride, cuprous chloride, stannous chloride, or other reducing agents.[1] The dilute solutions of the chloride have a violet colour, whilst the concentrated solutions or those containing a large excess of acid are green. Recoura[2] has shown that the heat evolved by the action of an equivalent quantity of soda is nearly 50 per cent. greater in the case of the green solutions, and that as the concentration of the solution increases, the evolution of heat gradually increases from the value for the violet solution (+22·2 Cal.) to that for the dark green (+31·5 Cal.). The colour of the solution at the same time gradually changes from violet to pure green, thus indicating a gradual transition of the violet into the green modification. It has also been shown[3] that equilibrium between the green and the violet salts is set up in solution, either salt leading to the same final conditions, depending on the concentration. In dilute solutions, the salt is almost all present in the violet form, $[Cr(H_2O)_6]Cl_3$, whilst as the concentration increases the equilibrium shifts more and more in favour of the green. The equilibrium is reached very slowly at the ordinary temperature, but may be attained in 24 hours at 84°. Both modifications have been isolated in the crystalline condition by Recoura, and both have the same composition, $CrCl_3,6H_2O$.[4]

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[1] For a detailed explanation of Werner's theories, see A. Werner, "*Neuere Anschauung auf dem Gebiete der anorganischen Chemie*" (4th edn., Braunschweig, 1920).

[2] Poulenc, *Compt. rend.*, 1891, 116, 253; Fabris, *Gazz.* 1890, 20, 582.

[3] Recoura, *Compt. rend.*, 1913, 157, 1525; Costăchescu, *Ann. Sci. Univ. Jassy*, 1914, 8, 16.

[4] Recoura, *loc. cit.*

[5] From chromite, see Badische Anilin- und Soda-Fabrik, Ger. Pat., 281990.

The dark green chloride, $[CrCl_2(H_2O)_4]Cl,2H_2O$, separates in small, emerald-green crystals when a current of hydrogen chloride is passed through a well-cooled, saturated solution of chromic chloride. If the crude chloride be dissolved in its own weight of water, warmed for a few minutes to 80°, and then cooled to 0°, the solution contains both the dark green and the violet salt, and on passing in hydrogen chloride, only the latter separates at first, and may be obtained free from the green modification if it be immediately filtered off. It forms greyish-blue crystals which dissolve in water, forming the characteristic bluish violet solution. Intermediate between the violet hexahydrate and the dark green hexahydrate is the light green hexahydrate,

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[1] Rohland, *Zeit. anorg. Chem.*, 1899, **21**, 37; *ibid.*, 1903, **29**, 159; Drucker, *Zeit. physikal. Chem.*, 1901, **36**, 173.

[2] Recoura, *Ann. Chim. Phys.*, 1887, [6], **10**, 5.

[3] Roozeboom and Olie, *Proc. K. Akad. Wetensch. Amsterdam*, 1906, **8**, 66; *Zeit. anorg. Chem.*, 1906, **51**, 29; Werner and Gubser, *Ber.*, 1901, **34**, 1379.

[4] Marchetti, *Gazz.*, 1882, **22**, 375.

$[CrCl(H_2O)_5]Cl_2,H_2O$, obtained by Bjerrum[1] by adding ether saturated with hydrogen chloride to the solution left after precipitating the violet salt with hydrochloric acid. It forms a light green, microcrystalline powder which is even more hygroscopic than the other isomers; on attempted drying it passes gradually into the dark green compound.[2] The latter substance, however, when kept in a desiccator, loses two molecules of water, forming a tetrahydrate, whilst a decahydrate is also known.[3] The constitution of these hydrates will be discussed in conjunction with that of the ammoniacal compounds of chromium (*q.v.*). Certain lower hydrates are stated to possess a red colour, as also does the compound $CrCl_3,3C_2H_5,OH$.

Basic chromic chlorides have been prepared,[4] the composition of which varies according to the method of preparation.[5]

Double compounds of an oxychloride of chromium with the chlorides of the alkali metals have been described, in which the chromium appears to be quinquevalent. Thus the potassium compound, $CrOCl_3,2KCl$, is formed as a garnet-red, crystalline precipitate when a solution of potassium chloride is added to a concentrated solution of chromic acid which has previously been treated with hydrochloric acid at −20°, and the mixture saturated at 0° with hydrogen chloride. Similar examples have been prepared with quinoline and pyridine hydrochlorides.[6]

Chromic Bromide, $CrBr_3$.—The anhydrous salt is prepared in a similar way to the chloride. It forms almost black, semi-metallic, translucent, hexagonal scales which in thin sections appear green by transmitted and red by reflected light. In its properties it closely resembles the chloride, and dissolves easily in water, when a small quantity of chromous bromide, or any other reducing agent, such as tinfoil, is present. Solutions of chromic bromide behave in an analogous manner to those of the chloride, and yield two isomeric salts, the one forming bluish-grey, and the other green crystals, both of which have the composition $CrBr_3,6H_2O$.[1] The former has the constitution $[Cr(H_2O)_6]Br_3$ and the latter is $[CrBr_2(H_2O)_4]Br,2H_2O$. An octahydrate also exists.

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[1] Bjerrum, *Ber.*, 1906, **39**, 1597; *Zeit. physikal. Chem.*, 1907, **59**, 581. See also Weinland and Schumann, *Zeit. anorg. Chem.*, 1908, **58**, 176.

[2] For double salts of these chlorides, see Larsson, *Zeit. anorg. Chem.*, 1920, **110**, 153; Weinland and Koch, *ibid.*, 1904, **39**, 296; Weinland and Schumann, *ibid.*, 1907, **40**, 3767.

[3] Werner and Gubser, *Ber.*, 1901, **34**, 1579; Olie, *Zeit. anorg. Chem.*, 1907, **53**, 268.

[4] Moberg, *J. pr. Chem.*, 1843, **29**, 175; Schiff, *Annalen*, 1862, **124**, 168; Olie, *Zeit. anorg. Chem.*, 1906, **52**, 62.

[5] For further information regarding the chromic chlorides, see; Elias, *Anal. Fis. Quim.*, 1918, **16**, 467; Feytis, *Compt. rend.*, 1913, **156**, 886; Wyrouboff, *ibid.*, 1913, **156**, 1072; Heydweiller, *Zeit. anorg. Chem.*, 1915, **91**, 66; Lamb and Fonda, *J. Amer. Chem. Soc.*, 1921, **43**, 1154; Hopfgartner, *Monatsh.*, 1919, **40**, 250; Baldwin, *J. Amer. Leather Chem. Assoc.*, 1919, **14**, 10; Kurilov, *Kolloid Zeit.*, 1914, **14**, 171.

[6] Meyer and Best, *Zeit. anorg. Chem.*, 1899, **22**, 92; Weinland and Fridrich, *Ber.*, 1905, **38**, 3784; Weinland and Fiederer, *Ber.*, 1906, **37**, 4042; 1907, **40**, 2090.

Chromic Iodide, $CrI_3,9H_2O$, forms unstable violet crystals.[2]

CHROMIUM AND SULPHUR.

479 *Chromium Sesquisulphide*, or *Chromic Sulphide*, Cr_2S_3.—This is obtained by heating chromium with sulphur, or by igniting chromic chloride, or the trioxide, in a current of hydrogen sulphide. It forms either a blackish-grey powder with a metallic lustre, or an elastic mass having a density of 3·77. When heated in the air it burns with formation of the green oxide, and in chlorine yields sulphur chloride and chromic chloride. This compound cannot be prepared in the wet way, as soluble sulphides precipitate the hydroxide from chromic salts, with liberation of sulphuretted hydrogen :

$$2CrCl_3 + 6H_2O + 3(NH_4)_2S = 2Cr(OH)_3 + 6NH_4Cl + 3H_2S.$$

Chromic Sulphate, $Cr_2(SO_4)_3$, is obtained by mixing equal parts of concentrated sulphuric acid and chromium hydroxide dried at 100°. The mixture is allowed to stand in a loosely-stoppered bottle, when the green solution becomes blue, and in some weeks deposits a violet-blue, crystalline mass, which is purified by solution in water and precipitation with alcohol. Thus obtained, it is a violet, crystalline powder; with less alcohol, blue octahedra containing 18 molecules of water are deposited. Chromic sulphate and the sulphates of the alkali metals form double salts, corresponding to the alums, to which the name of *chrome-alums* is given.

Potassium Chromic Sulphate, $K_2SO_4,Cr(SO_4)_3,24H_2O$, or *Chrome Alum* is best obtained by the reduction of a solution of potassium dichromate, $K_2Cr_2O_7$, by adding the requisite quantity of sulphuric acid, and passing sulphur dioxide through the solution :

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

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[1] Recoura, *Compt. rend.*, 1890, **110**, 1029. See also Hein, *Ber.*, 1919, **52**, [*B*], 195.

[2] Higley, *J. Amer. Chem. Soc.*, 1904, **26**, 613.

In place of sulphur dioxide any other easily oxidisable substance such as alcohol, etc., may be employed, but in this case more sulphuric acid must be added. Chrome alum is now obtained in large quantity as a by-product in the manufacture of artificial alizarin from anthracene, $C_{14}H_{10}$, in which the hydrocarbon is treated with a mixture of sulphuric acid and potassium dichromate, when anthraquinone, $C_{14}H_8O_2$, is formed, and this is then subjected to further treatment. The salt crystallises in large, dark purple-red, almost black octahedra, which, when seen by transmitted light, exhibit a ruby-red colour. One litre of water at 25° dissolves 243·9 grams of the crystalline salt; the solution has a dingy blue colour, with a tinge of red, which when heated to 70° becomes dark green. After standing for several months, however, it returns to its ordinary colour (see below). Chrome alum is used in dyeing and calico-printing as well as in tanning.

Ammonium Chromic Sulphate, $(NH_4)_2SO_4,Cr_2(SO_4)_3,24H_2O$, is obtained by crystallising a mixture of the two salts, or by reducing ammonium dichromate in presence of sulphuric acid. The salt is less soluble than the potassium compound, and crystallises readily in fine ruby-red octahedra, which effloresce in the air.

A number of other crystalline double chromic sulphates, both anhydrous and hydrated, have been described.[1]

Action of Heat on Chromic Sulphate and its Double Salts.—When the cold violet solution of chromic sulphate is boiled, there is produced a green solution which contains a considerable quantity of hydrogen ions; evidently hydrolysis has taken place, with the formation of soluble basic sulphates, probably of a complex, or even polymeric character. In such modified solutions, the sulphate is only partially ionised, since precipitation with barium chloride yields only a proportion of the anticipated quantity of barium sulphate. It is impossible to assign definite formulæ to such hydrolytic products, of which the composition is doubtless more complex than $[Cr_4O(SO_4)_4]SO_4$ or $[Cr_4(H_2O)_n(OH)_2(SO_4)_4]SO_4$ as suggested by Recoura and others.[2] By keeping at the ordinary temperature, these green solutions are gradually converted into the ordinary violet solutions. The double salts, such as chrome alum, undergo an analogous reaction when the solutions are heated.

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[1] Schrötter, *Pogg. Ann.*, 1841, **53**, 513; Carstanjen, *J. pr. Chem.*, 1867, **102**, 65; Pettersson, *Ber.*, 1876, **9**, 1559; Meyeringh, *ibid.*, 1877, **10**, 1946; Klobb, *Compt. rend.*, 1893, **117**, 311; *Bull. Soc. chim.*, 1893, [3], **9**, 663; Sommer, *Zeit. anorg. Chem.*, 1916, **96**, 70; Ephraim and Wagner, *Ber.*, 1917, **50**, 1088.

[2] Recoura, *Ann. Chim. Phys.*, 1895, [7], **4**, 494; Favre and Valson, *Compt. rend.*, 1872, **74**, 1023; Whitney, *Zeit. physikal. Chem.*, 1896, **20**, 40; Dougal, *J. Chem. Soc.*, 1896, **69**, 1526; Colson, *Compt. rend.*, 1905, **140**, 42, 372, 1451; **141**, 119, 331, 1024; 1906, **142**, 402; 1907, **144**, 79, 206, 325, 637; **145**, 250; *Bull. Soc. chim.*, 1907 [4], **1**, 438, 669; 1908, [4], **3**, 90; *Ann. Chim. Phys.* 1907, [8], **12**, 433. See also Meunier and Casto, *Compt. rend.*, 1921, **172**, 1488.

Green Modifications of Chromic Sulphate.—In addition to the above complex basic sulphate, a solid green salt of the same empirical formula as the normal violet salt is known, which, however, possesses entirely different properties.[1] This is obtained by heating the crystals of the violet salt, $Cr_2(SO_4)_3,18H_2O$,[2] at 90° until they have the composition $Cr_2(SO_4)_3,6H_2O$.[3] The resulting green compound is readily soluble in water, but the freshly prepared solution shows the ordinary reactions neither of a chromium salt nor of a sulphate; further, it is capable of "masking" the sulphate-ion of other sulphates to a considerable extent.[4] In the course of a few days the solution is gradually transformed into that of the normal violet sulphate. In dry air, the green sulphate yields $Cr_2(SO_4)_3,3H_2O$, and becomes anhydrous at 400°. According to Werner's views, green chromic sulphate hexahydrate is formulated, $[Cr_2(SO_4)_3(H_2O)_6]$, whereas the corresponding violet compound is formulated

$$[Cr_2(H_2O)_{12}](SO_4)_3,xH_2O.$$

It would be anticipated that intermediate salts of the form $[Cr_2(H_2O)(SO_4)_2](SO_4),aq.$ and $[Cr_2(H_2O)_2SO_4](SO_4)_2,aq.$, in which respectively one-third and two-thirds of the sulphate are precipitable by barium chloride would be found to exist. Colson's observation[5] that such salts may be prepared does not, however, appear to have received definite confirmation. Recoura[6] has reported the existence of a lilac-grey sulphate which appears to consist of 1 mol. of the green salt and 2 mols. of the normal violet salt. At first, the sulphate ions corresponding to the green sulphate are masked, whilst those corresponding to the violet salt are precipitable; on keeping, however, the latter sulphate ions also become masked. In explanation, the polymerisation of the green salt is put forward.

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[1] Recoura, *Ann. Chim. Phys.*, 1895, [7], **4**, 505. See also Cabrera and Marquina, *Anal. Fis. Quim.*, 1917, **15**, 199; Shibata and Matsuno, *J. Coll. Sci. Tokyo*, 1920, **41**, 6, 1.

[2] But see Sénéchal, *Compt. rend.*, 1913, **156**, 552.

[3] Wyrouboff, *Bull. Soc. chim.*, 1902, **27**, 666; Colson, *Compt. rend.*, 1907, **144**, 206; Kling, Florentin, and Huchet, *ibid.*, 1914, **159**, 60; Sénéchal, *ibid.*, 1914, **159**, 243.

[4] Recoura, *Compt. rend.*, 1922, **174**, 1460.

[5] Colson, *loc. cit.*

[6] Recoura, *Compt. rend.*, 1920, **170**, 1494. See also *ibid.*, 1919, **169**, 1163.

Although acid chromic sulphates are known,[1] Recoura has shown [2] that when the green sulphate combines with one, two, or three molecules of sulphuric acid or a sulphate, substances are obtained from which no barium sulphate can be obtained by precipitation in the cold, neither are chromium ions present; these may be regarded as the complex acids, *chromosulphuric acid*, $[Cr_2(SO_4)_4]H_2$, *chromodisulphuric acid*, $[Cr_2(SO_4)_5]H_4$, and *chromotrisulphuric acid*, $[Cr_2(SO_4)_6]H_6$, or their salts. These are stable in dry air, but in solution they gradually undergo conversion into the normal chromium salts. The alkali chromosulphates are isomeric with the chrome alums, from which they may be readily obtained by heating the crystals of the latter for some time at 90°. *Potassium chromosulphate*, $[Cr_2(SO_4)_4]K_2,4H_2O$, is thus obtained as a green salt which dissolves slowly but completely in cold water.

The colloidal character of the chromosulphuric acids has been demonstrated by Strong.[2]

An analogous series of acids has been prepared by the union of the green chromic sulphate with chromic acid. These have the compositions $[Cr_2(SO_4)_3,CrO_4]H_2$, $[Cr_2(SO_4)_3,(CrO_4)_2]H_4$, and $[Cr_2(SO_4)_3,(CrO_4)_3]H_6$, and are called the *chromosulphochromic acids*.[3]

Various complex *chromiselenates* have also been prepared.[4]

CHROMIUM AND NITROGEN, PHOSPHORUS, AND BORON.

480 *Chromium Nitride*, CrN, is formed by the direct union of its elements at a red heat;[5] and also by passing ammonia over heated chromic chloride. It is a brownish-black powder, which takes fire and burns when heated to 200° in the air or in oxygen. Cold chlorine does not act upon it, but when heated in this gas small explosions first occur owing to formation of nitrogen chloride, and finally chromic chloride remains. It does not undergo change on ignition in hydrogen or in aqueous vapour, and is not attacked

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[1] Weinland and Krebs, *Zeit. anorg. Chem.*, 1906, **49**, 157.

[2] Strong, *Compt. rend.*, 1910, **150**, 1172. These compounds, particularly those composed of 1 mol. of $Cr_2(SO_4)_3$ with 4, 5, and 6 mols. of H_2SO_4, can therefore no longer be regarded as compounds of the type called "sulphochromic hydroxide" by Recoura, *loc. cit.*, See also Calvert and Ewan, *Proc. Chem. Soc.*, 1896, **12**, 160.

[3] Recoura, *Bull. Soc. chim.*, 1897, [3], **17**, 934; *Ann. Chim. Phys.*, 1895, [7], **4**, 494.

[4] Meyer, *Zeit. anorg. Chem.*, 1921, **118**, 1.

[5] Briegleb and Geuther, *Annalen*, 1862, **123**, 239.

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y potassium hydroxide, hydrochloric acid, or nitric acid. Con-
entrated sulphuric acid converts it into the sulphates of
mmonium and chromium:

$$2CrN + 4H_2SO_4 = Cr_2(SO_4)_3 + (NH_4)_2SO_4.$$

Chromic Azide, $Cr(N_3)_3$, has been obtained[1] as well as its
yridine compound, $Cr(N_3)_3,3Py$, which is explosive, and the
mpound $CrN_9,3NaN_3$. Basic salts are known.

Chromic Nitrate, $Cr(NO_3)_3,9H_2O$, is obtained by dissolving the
ydroxide in nitric acid; it crystallises in oblique, purple-red
isms. The solution, like that of the sulphate, turns green on
iling, and on evaporation dries to a green, amorphous mass.
e green solution immediately becomes violet on cooling.

Chromium Phosphides.—By heating finely divided chromium
th red phosphorus in a sealed tube, the phosphide, Cr_2P_3, is
tained; when this compound is heated in hydrogen, chromic
osphide, CrP, is produced.[2] Both are grey substances which
e insoluble in acids.

Chromic Hypophosphite, $Cr(H_2PO_2)_3,2H_2O$, is a green mass
tained by dissolving freshly prepared chromic hydroxide in
pophosphorous acid.[3]

hromic Phosphates.—When a solution of sodium hydrogen
osphate is added to an excess of chrome alum solution a
atinous precipitate is formed which on keeping for forty-eight
urs is transformed into dark violet crystals of the phosphate,[4]
$rPO_4,6H_2O$; more prolonged contact with the precipitant yields
green, amorphous tetrahydrate. By boiling the violet salt with
water, the tetrahydrate is obtained in crystalline form, whereas
treatment with acetic anhydride yields a dihydrate. On ignition
of a hydrate, the anhydrous salt is obtained as a brown, amorphous
powder. If chromic hydroxide is dissolved in excess of phosphoric
acid and the solution evaporated and heated to 316°, *chromic
metaphosphate*, $Cr(PO_3)_3$, is obtained, which has been employed
as a green pigment. *Chromic pyrophosphate* in alkaline solution
gradually yields salts of the type $M'(CrP_2O_7),nH_2O$ (*chromi-
pyrophosphates*).[5]

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[1] Oliveri-Mandalà, *Gazz.*, 1919, **49**, ii, 43; 1922, **52**, i, 112; Wöhler and Martin, *Ber.*, 1917, **50**, 595.

[2] Dieckmann and Hanf, *Zeit. anorg. Chem.*, 1914, **86**, 291. See also Granger, *Compt. rend.*, 1897, **124**, 190; Maronneau, *ibid.*, 1900, **130**, 656.

[3] Mawrow and Zonew, *Zeit. anorg. Chem.*, 1915, **93**, 311.

[4] Schiff, *Zeit. anorg. Chem.*, 1905, **43**, 304; Joseph and Rae, *Trans. Chem. Soc.*, 1917, **111**, 190.

[5] Rosenheim and Triantaphyllides, *Ber.*, 1915, **48**, 582.

Chromium Arsenides.—The compounds Cr_2As_3 and CrAs have been prepared similarly to the phosphides.[1] An *arsenite, arsenates,* and a *metantimonate* have been described.

Chromium Borides.—Two chromium borides have been prepared by heating the elements together in the electric furnace;[2] these have the formulæ CrB, and Cr_3B_2, and are grey, crystalline substances.

CHROMIUM AND CARBON AND SILICON.

481 *Chromium Carbides.*—These fall into two groups:[3] (1) those containing up to 8·5 per cent. C, and (2) those containing a larger proportion of carbon. The former are completely soluble in hot 24 per cent. hydrochloric acid; the latter only partially. The carbide Cr_5C_2 forms silvery crystals of density 6·9. It melts at 1665° and is unattacked by aqua regia. The carbide Cr_3C_2 is darker in colour, has a density 6·68, and melts at about 1890° with partial decomposition to Cr_4C_2 and graphite. Moissan[4] has described carbides of the composition Cr_2C_3 and Cr_4C respectively.

Chromium Carbonate.—Chromic hydroxide absorbs carbon dioxide from air, yielding a compound to which the formula

$$(a)\ \begin{matrix} Cr_2(OH)_5\cdot O\diagdown \\ Cr_2(OH)_5\cdot O\diagup \end{matrix} CO,9H_2O \text{ or } (b)\ O\begin{matrix} \diagup Cr_2(OH)_4\cdot O\diagdown \\ \diagdown Cr_2(OH)_4\cdot O\diagup \end{matrix} CO,10H_2O$$

has been given.[5]

Cyanogen Compounds of Chromium.—*Chromous cyanide* is unstable in air. *Potassium chromocyanide,* $K_4[Cr(CN)_6],2H_2O$, is obtained by the action of potassium cyanide on chromous acetate, and forms blue crystals. It is soluble in water, and on exposure to air passes into

Potassium Chromicyanide or *Potassium Hexa-cyano-chromite,* $K_3[Cr(CN)_6]$, light yellow, monoclinic crystals, obtained also by pouring a solution of chromic acetate into a boiling solution of potassium cyanide.

A number of chromicyanides of other metals have also been prepared.[6]

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[1] Dieckmann and Hanf, *Zeit. anorg. Chem.*, 1914, **86**, 291.

[2] Tucker and Moody, *Journ. Chem. Soc.*, 1902, **81**, 16; Binet du Jassonneix, *Compt. rend.*, 1906, **143**, 897; Wedekind and Fetzer, *Ber.*, 1907, **40**, 297.

[3] Ruff and Fœhr, *Zeit. anorg. Chem.*, 1918, **104**, 27.

[4] Moissan, *Compt. rend.*, 1894, **119**, 185.

[5] Jovitschitsch, *Compt. rend.*, 1914, **158**, 872; *Helv. Chim. Acta*, 1920, **3**, 46.

[6] Fischer and Benzian, *Chem. Zeit.*, 1902, **26**, 49; Cruser and Miller, *J. Amer. Chem. Soc.*, 1906, **28**, 1132.

Chromic Thiocyanate, $Cr(SCN)_3$.—Chromic hydroxide dissolves in thiocyanic acid solution yielding a greenish-violet solution which when concentrated over sulphuric acid dries to a dark-green amorphous, deliquescent mass. It forms a series of characteristic double salts, which are regarded as salts of complex acid radicles containing chromium.[1] The complex ions present in such solutions are:[2] $[Cr\,aq_6]^{+++}$, $[Cr\,aq_5(CNS)]^{++}$, $[Cr\,aq_4(CNS)_2]^{+}$, $[Cr\,aq_3(CNS)_3]$ (non-electrolyte), $[Cr\,aq_2(CNS)_4]^{-}$, $[Cr\,aq(CNS)_5]^{--}$, and $[Cr(CNS)_6]^{---}$. Of particular importance is the potassium salt of the last-mentioned ion.

Potassium Chromithiocyanate or *Potassium Hexathiocyanochromite*, $K_3[Cr(SCN)_6],4H_2O$, is formed by heating a moderately concentrated solution of 6 parts of potassium thiocyanate and 5 parts of chrome alum for two hours at the boiling point; the sulphates formed are precipitated by the addition of alcohol, the filtrate evaporated, and the residues recrystallised from alcohol. It forms tetragonal, almost black crystals, which appear ruby-red by transmitted light, and dissolve very readily in water and alcohol, forming wine-red solutions. It is decomposed by alkalis and warm hydrochloric acid. The solution gives precipitates of analogous compounds with lead and silver salts.[3]

Chromium and Silicon.—Several silicides of chromium have been described; these are all prepared by heating chromium with silicon, or a mixture of silica and chromic acid with carbon or copper and aluminium in the electric furnace. In this way the compounds Si_2Cr, Si_2Cr_3, $SiCr_2$, and $SiCr_3$ have been obtained.[4] The compound, Si_2Cr_3, is also formed when silicon chloride is heated for some time in contact with chromium.[5]

Chromium and Tungsten.—Chromic tungstates and derivatives of tungsto-chromic acid are known.[6]

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[1] Rösler, *Annalen*, 1867, **141**, 185.

[2] Bjerrum, *Det. K. Danske Vidensk. Selskabs Skrifter, Nat. Math.*, 1915, 7, 60; *Zeit. anorg. Chem.*, 1921, **118**, 131; **119**, 39, 54, 179; see also Bohart, *J. Physical Chem.*, 1915, **19**, 537; Scagliarini, *Atti R. Accad. Lincei*, 1918, [5], **27**, i, 442.

[3] Rösler, *Annalen*, 1867, **141**, 185; Rosenheim and Cohn, *Zeit. anorg. Chem.*, 1901, **27**, 293.

[4] Moissan, *Compt. rend.*, 1895, **121**, 621; de Chalmot, *Amer. Chem. J.*, 1897, **19**, 69; Zettel, *Compt. rend.*, 1898, **126**, 833; Lebeau and Figueras, *ibid.*, 1903, **136**, 1329.

[5] Vigouroux, *Compt. rend.*, 1907, **144**, 83.

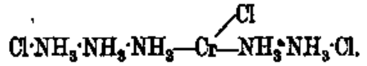
[6] See Kantschov, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 729.

AMMONIACAL AND OTHER COMPLEX COMPOUNDS OF CHROMIUM.

482 The salts of chromium readily combine with ammonia or substituted ammonias to form complex salts. These contain, for each atom of chromium, up to six molecules of ammonia, and often other elements or groups of elements united with the metal to form a complex radicle, which usually acts like a uni-, bi-, or ter-valent metal, but may in other cases have an acid function, or be neutral, that is, the complex is not ionised in aqueous solution. These complex salts are capable of undergong numerous double decompositions, giving rise to a large number of derivatives, among which many cases of isomerism occur. Analogous compounds are formed by other metals, in particular, cobalt and the metals of the platinum group, and these are to be regarded as included in the general statement which follows.

These compounds do not give the ordinary reactions of the metal, and in many cases this is also true of some or all of the acid radicles which they contain. This is accounted for, as already explained (pp. 37-38) by supposing that, in these latter cases, the acid radicle forms part of the complex group containing the metal, whereas those acid radicles which give the ordinary reactions are not contained in this group.

The constitution of these complex radicles is still under discussion, two different views being held. According to one of these (Blomstrand, Jörgensen) the metal retains its characteristic valency in all the compounds, the molecules of ammonia being attached to the metal in open chains by virtue of the pentavalent character of nitrogen. That portion of the acid radicles which does not retain its ordinary properties is directly connected with the metal, whilst the other portion is combined with nitrogen. Water may take the place of one or more of the ammonia groups, the oxygen atom being supposed to be quadrivalent. The compound $Cr(NH_3)_5Cl_3$, in which only two of the chlorine atoms are precipitable by silver nitrate in aqueous solution, would thus receive such a constitutional formula as



$$\mathrm{Cl{\cdot}NH_3{\cdot}NH_3{\cdot}NH_3{-}\overset{\diagup Cl}{Cr}{-}NH_3{\cdot}NH_3{\cdot}Cl.}$$

The existence of isomerides may be readily expressed by a variation in the arrangement of the various groups.

The second and more satisfactory view is that proposed by

Werner,[1] who classifies these compounds on the theory of principal and supplementary valency, an account of which has already been given (p. 37). The theory has naturally undergone modification in some details as experimental evidence has accumulated. According to this theory, in the compound $[Cr(NH_3)_6]Cl_3$, for example, the ammonia groups are all united or *co-ordinated* with the chromium atom by means of its supplementary valencies, whilst the chlorine, according to Werner's more recent view, is combined with the complex radicle as a whole, without being attached to any particular atom in it, and is said to be in *indirect combination* with this radicle. The ammonia groups may be either partially or entirely replaced by acid groups such as Cl, NO_2, SCN, etc., yielding a large number of compounds, which usually contain six groups in the complex radicle, although in some cases only four such groups can be present. The valency of the complex radicle is easily ascertained from the number and character of the groups within it. If the number of univalent acid radicles be less than the principal valency of the atom of the metal, the complex radicle is basic and capable of combining with a number of acid radicles equal to the difference. If, however, it be greater, the complex radicle has an acid character and is capable of combining with univalent basic radicles equal in number to the excess of the number of univalent acid radicles over the principal valency of the metal. When the number in the complex radicle is equal to the principal valency of the metal, the compound is a neutral substance.

This is illustrated in the following series of compounds derived from tervalent chromium, X representing a univalent acid and R a univalent basic radicle:

$[Cr(NH_3)_6]X_3$
$[Cr(NH_3)_5(SCN)]X_2$
$[Cr(NH_3)_4(SCN)_2]X$
$[Cr(NH_3)_3(SCN)_3]$
$[Cr(NH_3)_2(SCN)_4]R$
$[Cr(NH_3)(SCN)_5]R_2$ (unknown)
$[Cr(SCN)_6]R_3$

As already explained, the electrolytic dissociation and the reactions of these compounds in solution correspond with these formulæ.

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[1] *Annalen*, 1902, **322**, 261; *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (Vieweg & Sohn, *Braunschweig*, 1920). See also *Ber.*, 1907, **40**, 15, where an account of the literature on the subject is given. Recent investigations on the subject are described in papers by Jovitschitsch, *Monatsh.*, 1913, **34**, 225; Dubsky, *J. pr. Chem.*, 1914, [2], **90**, 61; Werner and others, *Annalen*, 1914, **405**, 212; **406**, 261; Mandal, *Ber.*, 1916, **49**, 1307; Briggs, *Journ. Chem. Soc.*, 1919, **115**, 67; Mandal, *Ber.*, 1919, **52**, [*B*], 330, 489; Frowein, *Zeit. anorg. Chem.*, 1920, **110**, 107.

In many cases, hydrated compounds of chromium may be formulated in a similar manner; instances have already been quoted in the cases of chromous chloride, chromic chloride, and chromic sulphate; Werner's formulation is in agreement with the behaviour of these substances in solution, when the whole or part only of the chloride or sulphate radicles is ionised. Examples may also be quoted of cases in which the ammonia groups in the complex radicle are only partially replaced by the "aquo" group, (OH_2), thus:

$$[Cr(NH_3)_6]Cl_3; \ [Cr(OH_2)(NH_3)_5]Cl_3, \text{ etc. } [Cr(OH_2)_6]Cl_3.$$

The bluish-violet chromic chloride hexahydrate is, of course, the final stage in such a substitution.

Compounds are also known, derived from the bivalent atom of the metal, in which the complex radicle contains six univalent acid groups, and is therefore capable of uniting with four basic radicles, examples being potassium chromocyanide, $[Cr''(CN)_6]K_4$, and potassium ferrocyanide, $[Fe''(CN)_6]K_4$.

The ammonia compounds are known as the *ammines*, this spelling of the word being adopted to avoid confusion with the organic *amines*, which have an entirely different constitution. The nomenclature of these compounds was originally founded on the colours characteristic of the various compounds, terms such as roseo-, praseo-, luteo-, croceo-, fusco-, xantho-, etc., having been employed. A much more rational method is due to Werner, the principle of which is that the names of the various groups contained within the complex radicle precede that of the metal, whereas those of the external group follow it, this being nothing more than an adaptation of the nomenclature frequently employed for organic compounds.

Thus the well-known cobalt compound, $[Cl(NH_3)_5Co]Cl_2$, formerly known as purpureocobaltic chloride, receives the name chloro-pentammine-cobaltic dichloride, whilst the compound $[(OH_2)(NH_3)_5Co]Cl_3$ (roseocobaltic chloride) becomes aquo-pentammine-cobaltic trichloride.[1]

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[1] Some of the metals from more than one series of complex derivatives, corresponding to the different series of simple salts. In order to distinguish these compounds, a special nomenclature has been introduced by Werner (*Neuere Anschauungen*, 1920, p. 92), according to which the valency of the metal is designated by the letters a-, o-, i-, e-, an-, on-, in-, en-, for uni-, bi-, ter-, quadri-, quinque-, sexa-, septa-, and octa-valent elements respectively. Thus among the complex halogen derivatives of the platinum metals, the compound $K_2[PtCl_4]$ is known as potassium tetrachloroplatinoate, $K_3[RhCl_6]$

Only a few examples of the chromium ammines are here described.[1] Amongst salts containing the chromium complex as the *anion* are:

6-(*Hexa*)*ammino-chromium salts*, $[Cr(NH_3)_6]X^{I}_3$ (luteo-salts), which are prepared by addition of ammonium chloride and ammonia to a solution of chromous chloride and allowing the cold mixtures to oxidise slowly.[2] Other members of this group are the ammino-aquo-chromium salts, in which some of the (NH_3) groups are replaced by (OH_2) groups. 5-Ammino-1-aquo (or aquopentammine)-chromium salts, formerly called roseo-salts, are included.

1-*Acido-5-ammino-chromium salts*, *e.g.*, $[CrCl(NH_3)_5]Cl_2$ (purpureo-salts). This compound is obtained, together with its mono-aquo-substitution derivative, $[Cr(OH_2)Cl(NH_3)_4]Cl_2$, by the action of liquid ammonia on violet chromic chloride. This group includes thiocyano-, nitrito-, nitrato-, etc., salts.

2-*Acido-4-ammino-chromium salts*, *e.g.*, $[CrCl_2\,en_2]Cl$,[3] obtainable in several different ways.

3-*Acido-3-ammino-chromium* compounds, *e.g.*, $[CrCl_3(NH_3)_3]$, are not ionised in aqueous solution. The compound given as an example of this class may be prepared by adding the compound $CrO_4{\cdot}3NH_3$ (see p. 1073) to cooled concentrated hydrochloric acid, filtering from a bluish-green precipitate, keeping the filtrate for two days, and separating the greenish-blue precipitate.

Compounds containing the chromium complex as the *kation*. 4-*Acido-2-ammino-chromites*, *e.g.*, $[Cr(SCN)_4(NH_3)_2]R'$.—When finely divided potassium dichromate is added to fused ammonium thiocyanate, ammonia is evolved, and the whole mass solidifies. When this is treated with water, filtered, and a few lumps of

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as potassium hexachlororhodiate and $K_2[PtCl_6]$ as potassium hexachloroplatineate. This system has been adopted to some extent in Germany, but has not come into general use in England. The neutral compounds are named as in the following examples: $[Co(NO_2)_3(NH_3)_3]$, trinitrotetramminocobalt; $[PtCl_2(NH_3)_2]$, dichlorodiamminoplatinum.

[1] For a full account of the compounds which have so far been prepared, reference must be had to Werner, *Neuere Anschauungen*, 1920; Abegg's "Handbuch der anorganischen Chemie, Vol. IV, (1), 2nd half; the literature quoted on page 1088, and the following papers: Weinland and Reihlen, *Zeit. anorg. Chem.*, 1913, **82**, 426; *Ber.*, 1913, **46**, 3144; Weinland and Ensgraber, *Zeit. anorg. Chem.*, 1913, **84**, 368; Barbieri, *Atti R. Accad. Lincei*, 1915, [5], **24**, i, 916; Weinland and Spanagel, *Ber.*, 1916, **49**, 1003.

[2] Jörgensen, *J. pr. Chem.*, 1884, [2], **30**, 1.

[3] The symbol "en" is used for the ethylenediamine group, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, corresponding to two ammonia groups.

ammonium chloride are added, garnet-red scales of the salt $[Cr(SCN)_4(NH_3)_2]NH_4$ separate.

5-*Acido*-1-*ammino-chromites* are unknown.

6-*Acido chromites*, $M'_3[CrX_6]$, no longer "ammines" since they contain no ammonia groups, include such compounds as the chromicyanides, chromioxalates, chromisulphates, etc.

A number of compounds have been described which contain organic amines, particularly ethylenediamine, and compounds such as pyridine, in the complex radicle in place of ammonia.

Isomerism of Complex Chromium Compounds.

A number of different types of isomerism[1] are known to which the complex chromium compounds are subject. It will be possible to mention each of these only very briefly.

1. *Polymerism.*—Certain complexes may be regarded as polymers of simpler ones, although widely different in constitution. Thus there are seven distinct compounds which possess the composition $Cr(NH_3)_3(SCN)_3$ or some multiple thereof.

2. *Co-ordination isomerism.*—Compounds with the same molecular formula may possess entirely different structural formulæ from the point of view of their ionisation and co-ordination relationships, *e.g.*,

$$[Co(NH_3)_6]^{\prime\prime\prime}\cdot[Cr(CN)_6]^{\prime\prime\prime} \text{ and } [Cr(NH_3)_6]^{\prime\prime\prime}\,[Co(CN)_6]^{\prime\prime\prime};$$
$$[Cr(NH_3)_6]\cdot[Cr(C_2O_4)_3] \text{ and } [Cr(NH_3)_4(C_2O_4)]\cdot[Cr(C_2O_4)_2(NH_3)_2].$$

3. *Hydrate isomerism*, as exhibited and already described in the case of chromic chloride, of which three isomeric forms exist, namely, $[Cr(OH_2)_6]Cl_3$ (violet), $[CrCl(OH_2)_5]Cl_2,H_2O$ (light green), and $[CrCl_2(OH_2)_4]Cl,2H_2O$ (dark green).

4. *Ionisation metamerism*, when different ions are furnished in aqueous solution, *e.g.*, the sulphate, $[Co(NO_3)(NH_3)_5]SO_4$, and the nitrate, $[Co(SO_4)(NH_3)_5]NO_3$.

5. *Salt isomerism* in which the differences exhibited are those between the salts of tautomeric acids, *e.g.*, nitrito- $(\cdot O\cdot N{:}O)$ and nitro- $\left(\cdot N{\ll}{}^{O}_{O}\right)$ groups.

6. *Structural isomerism*, *e.g.*, $[(NH_2)_2CS]_2\cdot Co(SCN)_2$ and $(NH_4SCN)_2\cdot Co(SCN)_2$, in which case the distinction is that between the thiocarbimido- and thiocyano-groups.

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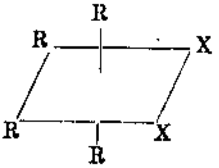
[1] This subject is discussed at some length in Werner's "*Neuere Anschauungen*," 1920, p. 327 *et seq.*

7. *Co-ordinative position isomerism, e.g.,*

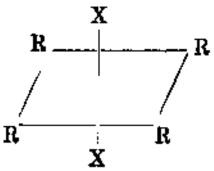
$$\left[Cl(NH_3)_3Co\begin{smallmatrix}NH_2\\ O_2\end{smallmatrix}Co(NH_3)_3Cl\right]Cl_2 \text{ and}$$

$\left[(NH_3)_4Co\begin{smallmatrix}NH_2\\ O_2\end{smallmatrix}Co(NH_3)_2Cl_2\right]Cl_2$. A similar difference exists between symmetrical and unsymmetrical dichloroethane, $CH_2Cl{\cdot}CH_2Cl$ and $CH_3{\cdot}CHCl_2$.

8. *Geometrical isomerism.*—As an example, complex radicles of the type $[MR_4X_2]$ may be cited. The metal atom is regarded as situated at the centre of a regular octahedron the corners of which are occupied by the co-ordinated groups. Two isomerides are then possible—the symmetrical or *trans*-form in which the groups X, X, are situated at opposite ends of a diagonal of the figure, and the asymmetrical or *cis*-form, in which they are at adjacent corners, thus:

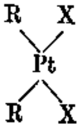


cis-Form. Asymmetric.

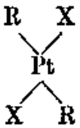


trans-Form. Symmetric.

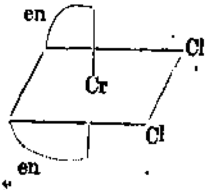
Of the same class are the platinous complexes, *e.g.*,

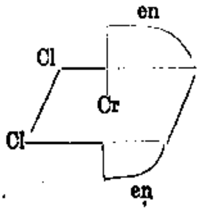


and



9. *Optical isomerism.*—There is no difference between the configuration of a *trans*-form and its mirror-image, but in the case of a *cis*-form it is possible to obtain two distinct configurations which are not identical, but bear to one another the relationship of mirror-images, thus:[1]





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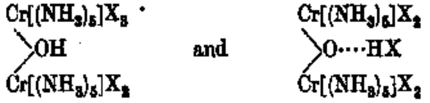
[1] The symbol "en" is used for ethylenediamine, $NH_2CH_2{\cdot}CH_2{\cdot}NH_2$, which corresponds to two ammonia groups.

10. *Valency isomerism, e.g.,*



$$\begin{matrix}\mathrm{Cr[(NH_3)_5]X_2} & & \mathrm{Cr[(NH_3)_5]X_2} \\ \rangle\mathrm{OH} & \text{and} & \rangle\mathrm{O\cdots HX} \\ \mathrm{Cr[(NH_3)_5]X_2} & & \mathrm{Cr[(NH_3)_5]X_2}\end{matrix}$$

where certain of the molecular components may be linked to a entral atom by either of the two types of valency (principal or uxiliary).

DETECTION AND ESTIMATION OF CHROMIUM.

483 *Chromous salts* in solution are unstable, readily becoming converted to green chromic salts with evolution of hydrogen; the solutions are therefore strong reducing agents. *Chromic salts* and the corresponding *sesquioxide* have a characteristic green or violet colour; with borax or microcosmic salt, both in oxidising and reducing flames, an emerald-green bead is produced. In aqueous solution, ammonia[1] gives a gelatinous precipitate of the hydroxide, $Cr(OH)_3$, which partially dissolves in excess of ammonia, yielding a violet solution which contains complex ammines; complete precipitation of the hydroxide is, however, attained from boiling solutions. By substitution of sodium or potassium hydroxide for ammonia, a solution of the chromic hydroxide, at first precipitated, in excess of the alkali is obtained; this is regarded both as a solution of a chromite and as a colloidal solution. On boiling, almost complete precipitation takes place: $Cr(OH)_3 + KOH \rightleftharpoons 2H_2O + CrO(OK)$.

Oxidation of green chromic salts to chromates having a characteristic yellow colour is readily effected. For qualitative purposes, it is sufficient to boil a solution of the salt with excess of sodium peroxide, sodium hypochlorite, or with nitric acid and lead dioxide,[2] but oxidation by fusion with a mixture of sodium carbonate and sodium peroxide conveniently admits of quantitative application.

The chromium salts do not impart any colour to the non-luminous gas flame. The spark spectrum of the metal is a complicated one, the brightest lines being 5208·8, 5207·4, 5204·7 in the green, and 4289·9, 4275·0, 4254·5 in the dark blue.[3]

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[1] Ammonium sulphide, or a mixture of potassium iodide and potassium iodate, may also be employed.

[2] Terni, *Gazz.*, 1913, **43**, ii, 63. See also Browning, *J. Amer. Chem. Soc.*, 1921, **43**, 114.

[3] The infra-red spectrum has been examined by Randall and Barker, *Astrophys. J.*, 1919, **49**, 54, and the X-ray spectrum by Fricke, *Physical Rev.*, 1920, **16**, 202.

Chromates.—If, after fusion of a chromic compound with sodium carbonate and sodium peroxide or potassium nitrate the melt is dissolved in water, the whole of the chromium is present, in solution as yellow sodium chromate, Na_2CrO_4; on acidification, such a solution darkens in colour owing to production of the dichromate, $Na_2Cr_2O_7$. The reverse reaction, of course, takes place when alkali is added to solutions of dichromates. From solutions of soluble chromates, barium chloride and lead nitrate precipitate the respective chromates which are yellow in colour; mercurous nitrate yields brown, amorphous, mercurous chromate which on boiling is converted into a red, crystalline form, some basic chromate also being produced. With normal chromates silver nitrate yields a brick-red precipitate, Ag_2CrO_4, whereas cold concentrated solutions of dichromates yield $Ag_2Cr_2O_7$, which is darker in colour. In presence of hydrogen sulphide, sulphurous acid, alcohol,[1] etc., chromates suffer reduction to green chromic salts, whilst in presence of hydrogen peroxide they are oxidised to perchromates. The latter reaction is very sensitive when carried out in dilute solutions in presence of sulphuric acid, blue perchromic acid being formed; although unstable in aqueous solution, the blue compound may be extracted with ether, in which it somewhat less rapidly decomposes. Another characteristic reaction of the chromates consists in the formation of red vapours of chromyl chloride, condensing to a red liquid, when a chromate is heated with a chloride and concentrated sulphuric acid. An intense blue coloration is, moreover, produced by α-naphthylamine in presence of tartaric acid.[2]

Estimation of Chromium.—Chromium may be estimated gravimetrically—in the case of the chromic salts as chromic oxide, and in the case of the chromates as mercurous chromate—or volumetrically by taking advantage of the oxidising action of chromates on ferrous salts, potassium iodide, etc. In view of the ease with which chromic salts are converted into chromates and *vice versâ*, the choice of the method suitable in any particular case is of the widest.

In order to estimate chromium gravimetrically in the chromic salts, a hot solution is precipitated with a very small excess of ammonia,[3] the solution boiled till the free ammonia is nearly all expelled, and the precipitate well washed with hot water, dried, ignited in a platinum crucible,[1] and weighed. Calcium and magnesium salts, if present, take part in the reaction with formation of insoluble chromites, but it has recently been stated[2] that these elements may be removed by washing the precipitate with a boiling 5 per cent. solution of ammonium nitrate.

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[1] For the photochemistry of this reaction, see Plotnikow, *Zeit. wiss. Photochem.*, 1919, **19**, 40.

[2] Van Eck, *Chem. Weekblad*, 1915, **12**, 6.

[3] The addition of 2 c.c. of 2½ per cent. tannic acid solution to the liquid before the addition of the ammonia greatly facilitates the subsequent filtration.

In the chromates, the gravimetric estimation of chromium is usually carried out by addition of mercurous nitrate to a solution made slightly acid with nitric acid, and boiling the mixture. The red, crystalline precipitate of mercurous chromate so obtained yields on ignition a residue of chromic oxide. Methods depending on the precipitation and weighing (as such) of silver, barium, and lead chromates have also been employed.

Soluble chromates may be estimated volumetrically by direct titration with ferrous salts, using potassium ferricyanide as an external indicator, or by an iodometric method,

$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 7H_2O + 3I_2,$$

the liberated iodine being titrated in the usual way with sodium thiosulphate solution. The valuation of chrome iron ore is commonly carried out by this method, the mineral being previously fused with an alkali and an oxidising agent, in order to convert the chromium into a soluble chromate.

It is possible to differentiate between chromate and dichromate when present together in solution by an acidimetric method.[3]

Atomic Weight of Chromium.—The older atomic weight determinations gave varying results, owing to the inexact methods and impure material employed. Berlin[4] obtained the number 52·5 by the analysis of silver chromate, whilst Kessler obtained 52·3 from the determination of the equivalent quantities of potassium dichromate and potassium chlorate required to oxidise arsenious oxide to pentoxide.[5] Siewert[6] found 52·07 by the analysis of violet chromic chloride and of silver dichromate, and Baubigny[7] got 52·14 by the conversion of chromic sulphate into the trioxide. Rawson,[8] by the conversion of pure ammonium dichromate into chromium trioxide, found the value 52·15, and Meineke[1] obtained the average figure 52·12 by estimating (1) the quantity of silver and chromium in silver chromate and ammonio-silver chromate; (2) the quantity of oxygen in these two compounds; (3) the quantity of oxygen in potassium dichromate; and (4) the quantity of oxygen and of chromium in ammonium dichromate. More recently, Baxter and others,[2] by reducing silver chromate or dichromate with sulphurous acid or hydrazine sulphate, and then precipitating the silver as chloride or bromide, have found 52·01 ± 0·01 for the atomic weight of chromium. The value now (1922) adopted is 52·0.

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[1] Rothang, *Zeit. anorg. Chem.*, 1913, **84**, 165; Schwarz, *Helv. Chim. Acta*, 1920, **3**, 330. It is necessary to avoid formation, not only of complex ammines, but also of chromic chromate.

[2] Toporescu, *Compt. rend.*, 1921, **172**, 600.

[3] Sacher, *Farbenzeit.*, 1916, **22**, 213.

[4] *Annalen*, 1844, **56**, 207; 1845, **60**, 182.

[5] *Pogg. Ann.*, 1861, **113**, 137.

[6] *Zeit. ges. Naturwiss.*, 1861, **17**, 630.

[7] *Compt. rend.*, 1884, **98**, 146.

[8] *Journ. Chem. Soc.*, 1889, **55**, 213.

MOLYBDENUM. Mo = 96·0. At. No. 42.

484 The name *Molybdæna*, which occurs in the writings of Dioscorides and Pliny, is derived from the Greek word μόλυβδος, lead, and was originally employed for the designation of a variety of substances containing lead. At a later time the name was used to signify galena or substances similar in appearance to this body, and to these the name of plumbago or black lead was also given. Even antimony sulphide and pyrolusite, to which latter mineral Linnæus gave the name *molybdænum magnesii*, were also classed among the same group of bodies. At a still later period this word was applied solely to graphite and to the mineral sulphide of molybdenum, which are very similar in appearance.

The difference between plumbago and the sulphide of molybdenum was first pointed out by Scheele in his treatise on "Molybdæna" in 1778, and in another on "Plumbago" in 1779.[3] By heating the former mineral with nitric acid he obtained sulphuric acid, together with a peculiar white earth which he recognised as an acid-forming oxide, and termed *acidum molybdænæ*, and he assumed that the mineral was a compound of this acid with sulphur. In 1781 Bergman suggested that the earth was probably a calx of a metal, and in 1782 he wrote that Hjelm had succeeded in preparing the metal, though the details of the experiments were first known in 1790.

Another mineral containing molybdenum is the yellow molybdate of lead or wulfenite first found in Carinthia. This was investigated by the elder Jacquin, and he showed that it contained lead, but was doubtful as to the nature of the acid with which this metal was combined. Salzwedel, who analysed it in 1790, believed that it was a lead tungstate, but Klaproth in 1797 ascertained its true composition. Later Berzelius more closely examined the molybdenum compounds.

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[1] *Annalen*, 1891, **261**, 339.

[2] *J. Amer. Chem. Soc.*, 1909, **31**, 529, 541.

[3] *Vetensk. Acad. Handl.*

Molybdenum is usually found as molybdenite, MoS_2, which occurs chiefly in Queensland and the United States; also as wulfenite, $PbMoO_4$. It occurs more rarely as molybdic ochre, which was for a long time believed to be molybdenum trioxide, MoO_3. Schaller,[1] however, from the analysis of a pure sample from Westmorland, New Hampshire, has shown it to be a hydrated ferric molybdate, $Fe_2O_3,3MoO_3,7\frac{1}{2}H_2O$. Iron ores frequently contain traces of molybdenum, and hence this metal is also found in pig-iron as well as in the slag. Thus the iron slag obtained in the process of melting the cupreous schist at Mansfield is said to contain from 9 to 28 per cent. of molybdenum.[2] Chillagite[3] has the composition $PbOWO_3,PbOMoO_3$ and powellite, $CaMoO_4$, in which a portion of the molybdenum is usually replaced by tungsten.

Metallurgy of Molybdenum.—Metallic molybdenum is obtained either electrically or by the "thermite" process.

By the electrical method, molybdenite is heated in a carbon tube with an arc of 350 amperes at 60 volts, when sulphur dioxide is evolved; the current is then increased to 900 amperes at 50 volts, when complete fusion takes place and the sulphur is entirely expelled. The metal prepared in this way, however, contains from 5 to 7 per cent. of carbon, which may be removed by heating with molybdic oxide. Molybdenum melts at 2450° ± 30°.[4]

A metal of 98 to 99 per cent. purity, containing some iron and very small quantities of silicon, is obtained by the reduction of molybdic oxide by means of aluminium powder.

Molybdenum is chiefly used in the form of rich ferromolybdenum alloys for the manufacture of special steels.[5] It also finds employment in the construction of certain electrical apparatus, and, in the form of molybdic acid, is used in analytical laboratories for the estimation of phosphorus.

[1] *Amer. J. Sci.*, 1907, [4], **23**, 207.

[2] Heine, *J. pr. Chem.*, 1836, **9**, 177.

[3] Ullmann, *J. Roy. Soc. N.S.W.*, 1912, **46**, 186; see also Cook, *Amer. J. Sci.*, 1922, [5], **4**, 50.

[4] Von Pirani and Meyer, *Zeit. Elektrochem.*, 1912, **18**, 137; Wolf, *Chem. Zentr.*, 1918, i, 608, gives the freezing point as 2250°.

[5] See Mennicke, *Elektrochem. Zeit.*, 1913, **20**, 181, 215, 250, 271; Aitchison, *Journ. Chem. Soc.*, 1915, **107**, 1531.

Metallic molybdenum may be obtained on the small scale as a grey powder, which assumes a silver-white appearance under pressure, by heating the trioxide or one of the chlorides in a current of hydrogen, but is best prepared by heating a mixture of molybdenum dioxide with one-tenth of its weight of sugar charcoal in a carbon crucible in the electric furnace, the action of the arc being stopped before the portions in contact with the crucible have had time to fuse. It is thus obtained free from carbon, whereas if too strongly heated it takes up the latter in considerable quantities. The pure metal is as malleable as iron, and is not hard enough to scratch glass, has a density[1] of 10·281, and can be forged when hot; it scarcely undergoes oxidation at the ordinary temperature, but is superficially attacked at a dull red heat, and rapidly at 600°, molybdenum trioxide subliming. It is rapidly attacked by fused potassium chlorate and nitrate. It may be distilled in the electric furnace, giving a vapour which solidifies in crystals.[2] When coarsely powdered it is attacked by fluorine at the ordinary temperature, by chlorine at a dull-red, and by bromine at a cherry-red heat, but not by iodine at the softening point of glass. When molybdenum filaments are heated in nitrogen, nitrides are probably formed.[3]

The metal is insoluble in dilute acids with the exception of nitric acid, but dissolves in concentrated sulphuric acid, the solution being first blue, but finally becoming colourless with formation of the trioxide, sulphur dioxide being also evolved. It is slowly attacked by fused alkalis. At high temperatures it is attacked by water vapour with liberation of hydrogen and formation of the dioxide.[4] In the potential series, molybdenum falls between Hg^{I} and $\mathrm{Sb}^{\mathrm{III}}$.

Molybdenum forms amalgams which may be obtained by the electrical method. When these amalgams are distilled *in vacuo*, molybdenum is left behind in the pyrophoric state.[5]

Although not obtainable by reduction of its compounds, molybdenum in a *colloidal* form has been prepared by an electrical dispersion method.[6]

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[1] Müller, *J. Amer. Chem. Soc.*, 1915, **37**, 2046; but Wolf, *Chem. Zentr.*, 1918, i, 608, gives 8·95.

[2] Moissan, *Compt. rend.*, 1906, **142**, 425.

[3] Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 167.

[4] See Chaudron, *Compt. rend.*, 1920, **170**, 182, 1056.

[5] Férée, *Compt. rend.*, 1896, **122**, 733.

[6] Svedberg, "Herstellung kolloider Lösungen anorganischer Stoffe" (Dresden, 1909).

MOLYBDENUM COMPOUNDS.

MOLYBDENUM AND OXYGEN.

485 Molybdenum combines with oxygen to form:

Molybdenum sesquioxide, Mo_2O_3,
Molybdenum dioxide, MoO_2,
Molybdenum trioxide, MoO_3.

The first two are basic oxides, but very little is known of their salts other than the halogen derivatives, the complex thiocyanates of the first, and the complex cyanides of the second. The trioxide is the most important, and like the analogous chromium oxide is an acid-forming oxide giving rise to the important series of *molybdates*. A blue oxide, which is usually regarded as a combination of the dioxide with the trioxide, is also known, but its composition is not definitely settled, whilst an oxide, Mo_2O_5, and a peroxide have also been described.

The compound formerly described as a hydrated monoxide has been shown to be the hydroxide of molybdenum sesquioxide; nor are simple salts of the hypothetical monoxide known, but only polymolecular complexes.

Molybdenum Sesquioxide, Mo_2O_3, is stated to be formed as a black substance when one of the higher oxides is treated with sodium amalgam, zinc, etc., but it is doubtful whether the product really has the composition Mo_2O_3. It is also formed by heating the metal in air or water vapour. The *hydroxide*, $Mo(OH)_3$, is first obtained as a brownish-black powder by precipitating with ammonia, washing with dilute ammonia, and drying in a current of hydrogen at 100°. When gently ignited in absence of air, the water evolved causes partial oxidation. A black precipitate of this hydroxide is also produced when molybdenum dichloride is boiled with caustic potash, hydrogen being evolved during the reaction.[1] The hydroxide is also reported to have been prepared by an electrolytic method,[2] and by reduction of ammonium paramolybdate in solution by hydrogen in presence of colloidal palladium.[3] Molybdenum sesquioxide is insoluble in acids, and even the hydroxide dissolves only with difficulty.

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[1] Muthmann and Nagel, *Ber.*, 1898, **31**, 2009.

[2] Smith and Hoskinson, *Amer. Chem. J.*, 1885, **7**, 90; Wolf, *Chem. Zentr.*, 1916, i, 608.

[3] Paal and Büttner, *Ber.*, 1915, **48**, 220.

Salts of the Sesquioxide.—With the exception of the metaphosphate, simple salts are not known in the crystalline form, although solutions of the hydroxide in acids yield amorphous residues on evaporation. A complex pyrophosphate [1] and oxalate containing tervalent molybdenum have, however, been prepared.

Molybdenum Dioxide, MoO_2, is formed when the sesquioxide is gently heated in a current of air, or when sodium trimolybdate is ignited for several hours in a current of hydrogen. It is the only oxide formed when molybdenum trioxide is reduced by heating in hydrogen,[2] and may be prepared pure by heating this oxide first at 470° in a stream of the gas, and then in a current of dry hydrogen chloride, when any unchanged trioxide is converted into a volatile oxychloride and thus removed.[3] It is formed also when ammonium molybdate is heated alone or fused with molybdenum trioxide,[4] and the product may be purified by washing successively with caustic soda, hydrochloric acid, and water, and then dried at 110°. The pure oxide is a brown or violet-brown, crystalline powder, and is reduced directly to the metal when heated at 600° in hydrogen. It is obtained in dark blue prisms resembling indigo by fusing sodium trimolybdate with one-third of its weight of zinc, and extracting the mass alternately with caustic potash and hydrochloric acid; [5] this product, however, always contains a little admixed zinc molybdate, but it may be obtained pure by fusing together 8 grams of fused ammonium molybdate, 14 grams of potassium carbonate, and 7 grams of boron sesquioxide, and extracting the cooled melt with water. It then forms opaque tetragonal crystals, having a violet reflex, and is insoluble in boiling hydrochloric acid and caustic potash.[6]

Molybdenum Tetrahydroxide, $Mo(OH)_4$.—It is probable that by interaction of alkalis with solutions of the reduction products of molybdic acid, only impure molybdenyl hydroxide, $MoO(OH)_3$, has been obtained, and not the tetrahydroxide as claimed. If, however, ammonium paramolybdate in aqueous solution is reduced at ordinary temperatures with hydrogen in presence of colloidal palladium, a greenish-black precipitate is obtained which has a composition corresponding approximately to

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[1] Rosenheim and Triantaphyllides, *Ber.*, 1915, **48**, 582.

[2] Guichard, *Compt. rend.*, 1839, **129**, 722.

[3] Friedheim and Hoffmann, *Ber.*, 1902, **35**, 791.

[4] Guichard, *Compt. rend.*, 1899, **129**, 722; 1900, **131**, 998.

[5] Ullik, *Annalen*, 1867, **144**, 227.

[6] Muthmann, *Annalen*, 1887, **238**, 114.

$MoO(OH)_2$.[1] By a modification of the procedure, the compound can be prepared in a colloidal form.[2]

Salts of the Dioxide.—With the exception of the chloride, bromide, and sulphide, which are prepared by dry methods, and possibly the fluoride and iodide, these are known with but little certainty; even in solution there is liability of confusion between the salts in question and a mixture of those of quinquevalent and tervalent molybdenum. On the other hand, a fairly large number of complex cyanides containing quadrivalent molybdenum have been prepared.

Molybdenum Pentahydroxide and the Oxide, Mo_2O_5.—It has already been mentioned that claims of the earlier investigators to have prepared the tetrahydroxide by interaction of alkalis with the reduction products of molybdic acid have not been substantiated, but that more or less impure molybdenyl hydroxide, $MoO(OH)_3$, the hydroxide of quinquevalent molybdenum, results. Klason[3] prepared the compound, by treating ammonium molybdenum oxychloride, $(NH_4)_2Mo_VOCl_5$, with ammonia, as a brown substance which gives a colloidal solution with water. It is insoluble in alkali hydroxide solutions, but soluble in those of alkali carbonates, though it possesses no acid properties.[4]

When the hydroxide is heated in a stream of carbon dioxide, a residue of the oxide, Mo_2O_5, is obtained as a violet-black powder. The existence of pure compounds of this composition is, however, doubtful.

Among other compounds containing quiquevalent molybdenum must be mentioned the pentachloride, the double thiocyanates, the sulphate, $Mo_2O_3(SO_4)_2$, and a series of complex oxalates. Barbieri[5] has prepared double molybdyl formates and oxalates containing the radicle Mo^VO_2.

MOLYBDENUM TRIOXIDE AND MOLYBDIC ACID.

486 *Molybdenum Trioxide*, MoO_3, was supposed to occur as molybdic ochre, but this has been shown to be hydrated ferric

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[1] Paal and Brünjes, *Ber.*, 1914, **47**, 2214; Paal and Büttner, *Ber.*, 1915, **48**, 220.

[2] See also Freundlich and Leonhardt, *Koll. Chem. Beihefte*, 1915, **7**, 172.

[3] Klason, *Ber.*, 1901, **34**, 148.

[4] Mawrow and Nikolow, *Zeit. anorg. Chem.*, 1915, **93**, 135, disagree with this statement.

[5] Barbieri, *Atti R. Accad. Lincei*, 1916, [5], **25**, i, 775.

molybdate. Gagarine[1] states, however, that he has found pure molybdic oxide as white or grey pseudomorphs after molybdenite in specimens from the Ilmen Mountains. It has a pearly lustre and is semi-transparent. It has probably been obtained by the oxidation of molybdenite which occurs there as pure sulphide without a trace of iron.

In order to prepare the trioxide in the pure state on the small scale the native sulphide may be heated in a combustion tube in a current of air until it is all oxidised and the trioxide sublimed.[2] On the larger scale, it may be obtained by mixing the same powdered mineral with an equal weight of pure quartz sand, and roasting the mixture on a flat iron plate. The roasted product is then boiled with dilute ammonia, and a small quantity of ammonium sulphide added to the solution in order to precipitate the copper. The filtered liquid is then evaporated to dryness, and the residue again dissolved in dilute ammonia. Crystals of ammonium molybdate are obtained from the filtrate on concentration. These are decomposed by nitric acid, evaporated to dryness, and the residual trioxide well washed with water. Molybdenum trioxide can also be obtained from native lead molybdate by first treating the mineral with dilute hydrochloric acid in order to remove iron, zinc, etc., then decomposing it with hot concentrated hydrochloric acid, evaporating down and digesting with dilute ammonia, when ammonium molybdate remains in solution and can be crystallised out as already described.[3] The ammonium molybdate may also be converted into the trioxide by being ignited in a platinum dish and subsequently heated to a dull red heat in a current of oxygen.[4]

Molybdenum trioxide is a white, impalpable powder, which when heated becomes yellow; it melts[5] at 795° to a dark yellow liquid, which, on cooling, solidifies to a yellowish-white, fibrous, crystalline mass, having a density of 4·696. It volatilises at very high temperatures when heated in closed vessels, but in the air it sublimes more easily, depositing small, colourless, transparent, rhombic tablets. It dissolves in 500 parts of cold, and in about 960 parts of hot water. The solution reddens litmus paper, turns turmeric paper brown, and possesses a sharp metallic taste.

Molybdic Acid, H_2MoO_4,H_2O or $MoO_3,2H_2O$, crystallises out in yellow crusts when three parts of ammonium molybdate are dissolved in twenty parts of water, the same quantity of nitric acid of specific gravity 1·16 is added, and the whole set aside. The deposition of the acid frequently takes place only very slowly, and the addition of a crystal of the compound renders its separation more easy.[1]

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[1] *Bull. Acad. Sci. St. Petersbourg*, 1907, 287.

[2] Wöhler, *Annalen*, 1856, **100**, 376.

[3] Wöhler, *Mineralanalyse*, 146.

[4] Muthmann, *Annalen*, 1887, **238**, 117.

[5] Jaeger and Germs, *Zeit. anorg. Chem.*, 1921, **119**, 145.

When the solution of the trioxide in nitric acid is allowed to evaporate spontaneously, a white, crystalline powder separates, which on heating loses water (Berzelius). This consists of the anhydrous acid, H_2MoO_4, which was once obtained by Ullik in the form of thin, prismatic crystals by the decomposition of magnesium molybdate with nitric acid. It is also formed when the yellow acid is heated at 60°, or its solution in water concentrated at 40–50°, and is thus obtained in white needles which are very sparingly soluble in cold, but more readily in hot water.[2] Two forms are distinguished as the α- and β-forms respectively.

Colloidal Molybdic Acid.—When the hydrochloric acid solution of ammonium molybdate is dialysed, a yellow, strongly acid, astringent solution of molybdic acid remains, which on evaporation yields a deliquescent, gummy mass.[3] After drying over sulphuric acid for several weeks it has the empirical formula $H_2Mo_2O_7$, but the determination of the molecular weight by Raoult's method indicates that it contains four MoO_3 groups.[4] If ordinary ammonium molybdate is precipitated with barium chloride, and the washed precipitate decomposed with the exact quantity of sulphuric acid, a colourless solution is obtained, possessing an acid reaction and metallic taste. When dried over sulphuric acid for several months it has the composition $H_2Mo_2O_7$, and on heating at 100°, 120°, and 160–170°, the residues have the compositions $H_2Mo_2O_7$, $H_2Mo_4O_{13}$ and $H_2Mo_8O_{25}$ respectively; at 250° pure molybdenum trioxide remains behind. Colloidal molybdic acid is rapidly reduced to the blue oxide by alcohol.

Molybdenum trioxide generally behaves as an acid-forming oxide analogous to chromium trioxide, and unites with bases to form molybdates. The normal molybdates are unstable, and show a great tendency to form polymolybdates corresponding to the polychromates by uniting with further molecules of the trioxide, as many as ten molecules of MoO_3 combining with one equivalent of a basic oxide.

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[1] Gmelin-Kraut, **2**, 171; Rosenheim and Bertheim, *Zeit. anorg. Chem.*, 1903, **34**, 427; 1906, **50**, 320; Graham, *Journ. Franklin Inst.*, 1907, **164**, 69.

[2] Rosenheim and Davidsohn, *Zeit. anorg. Chem.*, 1903, **37**, 314; Burger, *ibid.*, 1922, **121**, 240.

[3] Graham, *Journ. Chem. Soc.*, 1864, **19**, 326; See, however, Bruni and Pappadà, *Gazz.*, 1901, **31**, i, 244; Rosenheim and others, *loc. cit.*

[4] Sabanéef, *Journ. Chem. Soc.*, 1890, **58**, 1215.

The molybdates also combine with other acidic oxides, forming the series of salts known under the general term of the complex molybdates. The best known of these are the phosphomolybdic acids, in which a varying number of molecules of molybdenum trioxide and of phosphoric anhydride are combined with a basic oxide; similar compounds are formed by the acidic oxides of arsenic, sulphur, vanadium, antimony, and also of iodine, tin, silicon, and manganese.[1] The exact constitution of these salts is not yet known.

Molybdenum trioxide acts towards strong acids as a basic oxide; thus it combines with two molecules of hydrochloric acid to form a volatile crystalline compound, which is probably the *hydroxychloride*, $MoO(OH)_2Cl_2$; with sulphuric acid it yields the compound[2] MoO_2SO_4, analogous to the salts formed by the trioxides of tungsten and uranium.

Salt formation between molybdenum trioxide and bases is attended by the formation of a series[3] of compounds of complex constitution. Thus there may be formed substances of the type:

$R_2O{\cdot}MoO_3$ (normal molybdates)
$R_2O{\cdot}2MoO_3$ (di-molybdates)
$5R_2O{\cdot}12MoO_3$ (para-molybdates)[4]
$R_2O{\cdot}3MoO_3$ (tri-molybdates)
$R_2O{\cdot}4MoO_3$ (tetra-molybdates)
$R_2O{\cdot}8MoO_3$ (octa-molybdates)[5]
$R_2O{\cdot}10MoO_3$ (deca-molybdates)
$R_2O{\cdot}16MoO_3$ (hexakaideca-molybdates)

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[1] Péchard, *Compt. rend.*, 1901, **132**, 628; Rosenheim and Itzig, *Zeit. anorg. Chem.*, 1898, **16**, 76; Friedheim and Samelson, *Zeit. anorg. Chem.*, 1900, **24**, 65; Rosenheim and Liebknecht, *Annalen*, 1899, **304**, 40; Asch, *Zeit. anorg. Chem.*, 1901, **28**, 273. See also: Rosenheim and Jaenicke, *Zeit. anorg. Chem.*, 1912, **77**, 239; Copaux, *Compt. rend.*, 1913, **156**, 1771; Mazzucchelli and Ranucci, *Gazz.*, 1914, **44**, ii, 116; Rosenheim, Weinberg, and Pinsker, *Zeit. anorg. Chem.*, 1913, **84**, 217; Rosenheim and Traube, *ibid.*, 1915, **91**, 75; Prandtl and von Blochin, *ibid.*, 1915, **93**, 45; Mawrow and Nikolow, *ibid.*, 1915, **93**, 170; Weinland and Gaisser, *ibid.*, 1919, **108**, 231; Weinland and Zimmermann, *ibid.*, 1919, **108**, 248; Forsén, *Compt. rend.*, 1921, **172**, 681; Darmois, *ibid.*, 1921, **172**, 1486; Posternak, *ibid.*, 1921, **172**, 597; Tanret, *ibid.*, 1921, **173**, 43.

[2] Compare Guichard, *Compt. rend.*, 1906, **142**, 744.

[3] Forsén, *Compt. rend.*, 1921, **172**, 215, 327.

[4] Rosenheim, *Zeit. anorg. Chem.*, 1916, **96**, 139; but Copaux, *Compt. rend.*, 1913, **156**, 1771; Posternak, *ibid.*, 1920, **171**, 1058, regard paramolybdates as of the form $3R_2O{\cdot}7MoO_3$.

[5] Rosenheim, Felix, and Pinsker, *Zeit. anorg. Chem.*, 1913, **79**, 292, regard octamolybdates as hydrogen-tetramolybdates.

The di-, para-, and tri-salts are sometimes called "isopoly" salts; tetra- and octa-salts, possibly derived from a sexabasic heteropoly-acid, are grouped as "meta" salts.

Sodium Molybdates.—The normal molybdate, Na_2MoO_4, is formed by fusing the trioxide with the requisite quantity of sodium carbonate, and crystallises from water in acute rhombohedra, containing two molecules of water; below 6° prisms containing 10 molecules of water separate, resembling Glauber's salt in appearance; these effloresce in the air, forming the first named salt. The *dimolybdate*, $Na_2Mo_2O_7$, is formed when sodium carbonate and the trioxide are fused in the requisite proportions, and is a crystalline mass soluble with difficulty in cold and only slowly in hot water. A solution yields the hexahydrate. *Sodium paramolybdate*, $5Na_2O,12MoO_3,36H_2O$, to which Rosenheim ascribes the formula[1] $Na_5H_5[H_2(MoO_4)_6],15{\cdot}5H_2O$ is obtained by allowing a solution of the calculated quantity of the trioxide in sodium carbonate or sodium hydroxide solution to evaporate spontaneously. On heating it loses water, with eventual loss of its individuality. The *trimolybdate*, $Na_2Mo_3O_{10},7H_2O$, obtained in a similar manner, crystallises in large needles, 3·9 parts of which dissolve in 100 parts of water at 20°, and in 137 parts at 100°. Other hydrates have been described. The *tetramolybdate*, $Na_2Mo_4O_{13},6H_2O$,[2] is prepared by the action of the calculated quantity of hydrochloric acid on the normal salt, and forms small, glistening crystals soluble with difficulty in cold, but readily in hot water. *Sodium octamolybdate*, $Na_2Mo_8O_{25},17H_2O$, is formed as clear, lustrous, monoclinic crystals when a solution of the normal molybdate spontaneously evaporates in presence of the calculated quantity of hydrochloric acid. A sodium octamolybdate crystallising with $15H_2O$ is said to be obtained by the action of sulphur dioxide on a solution of the tetramolybdate.[3] The *decamolybdate*, $Na_2Mo_{10}O_{31},12H_2O$, is a white, crystalline powder obtained by heating the normal salt on the water-bath with sufficient hydrochloric acid to saturate the requisite quantity of sodium. It is sparingly soluble in water. Salts containing $6H_2O$ and $22H_2O$ have also been prepared.[4] The compound

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[1] Rosenheim, *Zeit. anorg. Chem.*, 1916, **96**, 139; various other formulæ have, however, been ascribed; in particular, $3Na_2O,7MoO_3,22H_2O$.

[2] But see Rosenheim and Felix, *Zeit. anorg. Chem.*, 1913, **79**, 292. See also Wempe, *ibid.*, 1912, **78**, 298.

[3] Rosenheim, *Zeit. anorg. Chem.*, 1897, **15**, 180.

[4] Ullik, *Annalen*, 1870, **153**. 373; Rosenheim and Davidsohn, *Zeit. anorg. Chem.*, 1903, **37**, 314; Rosenheim, and Felix, *loc. cit.*; Rosenheim, Felif and Pinaker, *loc. cit.*

$Na_2Mo_{14}O_{43},9H_2O$ was obtained by Ullik[1] by boiling a solution of the normal molybdate with nitric acid. It may probably be regarded as an acid salt of a lower type.

Potassium Molybdates.—The normal salt, K_2MoO_4, obtained in a similar manner to the sodium salt, crystallises in microscopic four-sided crystals, which are readily soluble in water. It is trimorphous.[2] When hydrochloric acid is added drop by drop to a solution of the trioxide in potassium carbonate until a permanent turbidity is produced, the *paramolybdate* of the composition $K_6Mo_7O_{24},4H_2O$ (or $5K_2O,12MoO_3,8H_2O$) separates out on standing, in monoclinic prisms; it is decomposed by water into the *trimolybdate*, $K_2Mo_3O_{10},3H_2O$, which forms silky, pliable needles.[3] By heating a solution of sodium octamolybdate with potassium chloride, the *tetramolybdate*, $K_2Mo_4O_{13},7H_2O$, is obtained. A crystalline *octamolybdate*, $K_2Mo_8O_{25},13H_2O$, and hydrates of the *decamolybdate*, $K_2Mo_{10}O_{31}$, are also known (Rosenheim).

Ammonium Molybdates.—The *normal molybdate*, $(NH_4)_2MoO_4$, is produced when molybdenum trioxide or an ammonium polymolybdate is heated with excess of concentrated ammonia, and crystallises in four-sided prisms which are decomposed by water. The *dimolybdate*, $(NH_4)_2Mo_2O_7$, separates out on evaporating the mother-liquor of the normal salt, in the form of a white, crystaline powder.[4] When a solution of the trioxide in ammonia is evaporated, the compound $(NH_4)_6Mo_7O_{24},4H_2O$ (Delafontaine) crystallises out in large, colourless, monoclinic crystals. This is the salt usually known as ammonium molybdate. According to Klason,[5] however, the molecular weight in aqueous solution, taking into account the degree of dissociation indicated by the electrical conductivity, shows that this salt is probably a double salt, $(NH_4)_3H_3Mo_3O_{12},(NH_4)_2H_4Mo_3O_{12}$, which is resolved into its constituents, triammonium and diammonium trimolybdates, when dissolved in water. On the other hand, Junius[6] gives the formula as $(NH_4)_{10}Mo_{12}O_{41}$. Results of physico-chemical measurements show that in aqueous solution the anion is $Mo_{12}O_{41}$, consequently this would appear to be the correct formula.[1] The *trimolybdate*, $(NH_4)_2Mo_3O_{10},H_2O$, is frequently formed by the decomposition of a solution of the ordinary salt at a low temperature, when it separates out in silky needles, sparingly soluble in cold, but readily so in hot water. It may also be formed by interaction of a solution of the ordinary paramolybdate with a suitable quantity of hydrochloric acid. Other crystalline ammonium salts have been described, which contain a larger proportion of molybdenum trioxide.[2]

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[1] Ullik, *loc. cit.*

[2] Hüttner and Tammann, *Zeit. anorg. Chem.*, 1905, **43**, 215; Amadori, *Atti R. Accad. Lincei*, 1914, [5] **23**, i, 800; van Klooster, *Zeit. anorg. Chem.*, 1914, **85**, 49.

[3] Forsén, *Compt. rend.*, 1921, **172**, 215, 327, reports the existence of two potassium trimolybdates of the same degree of hydration.

[4] Compare Klason, *Ber.*, 1901, **34**, 153.

[5] *Ber.*, 1901, **34**, 153.

[6] *Zeit. anorg. Chem.*, 1905, **46**, 428.

Calcium Molybdate, $CaMoO_4$, is obtained by precipitating a solution of the ordinary ammonium salt containing an excess of ammonia with calcium chloride. It forms a white precipitate consisting of microscopic tetragonal pyramids. If calcium carbonate is boiled with an excess of the trioxide and water, and the solution allowed to evaporate spontaneously, *calcium trimolybdate*, $CaMo_3O_{10},6H_2O$, is deposited. The salt $H_2CaMo_8O_{26},17H_2O$ crystallises from a solution of the normal salt in the requisite quantity of hydrochloric acid. It is deposited in small, oblique, glistening prisms which are scarcely soluble in cold but readily dissolve in hot water.

Barium Molybdate, $BaMoO_4$, is obtained in tetragonal pyramids by fusing together sodium molybdate, barium chloride, and common salt, and is difficultly soluble in acids.

When the ordinary ammonium salt is precipitated with barium chloride, a flocculent precipitate of $Ba_3Mo_7O_{24},9H_2O$ or possibly $5BaO,12MoO_3,xH_2O$, is thrown down, which is slightly soluble in water. A compound, $BaMo_3O_{10},3H_2O$, having properties similar to the last salt, is obtained by precipitating a soluble trimolybdate. When barium carbonate is dissolved in soluble molybdic acid and the solution kept, oblique prisms of the salt $H_2BaMo_8O_{26},17H_2O$ are deposited; and if the normal salt be treated with dilute nitric acid the compound $BaMo_9O_{28},4H_2O$ is formed. This is insoluble in water and is not completely decomposed by acids, even by sulphuric acid.

Magnesium Molybdate, $MgMoO_4,5H_2O$, is obtained by boiling magnesia with water and molybdenum trioxide, and evaporating the solution, when the salt separates out in long, glistening, transparent prisms. A heptahydrate is also known. Magnesium molybdate forms with the molybdates of potassium and sodium double salts such as $K_2MoO_4,MgMoO_4,2H_2O$, which appear to be isomorphous with the corresponding manganese and ferrous salts. Magnesium forms para-, tri-, octa-, and 16-molybdates.

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[1] Sand and Eisenlohr, *Zeit. anorg. Chem.*, 1907, **52**, 68; Rosenheim, *ibid.*, 1910, **96**, 139; Posternak, *Compt. rend.*, 1920, **171**, 1058.

[2] Klason, *Ber.*, 1901, **34**, 153; Rosenheim, *Zeit. anorg. Chem.*, 1897, **15**, 180; 1903, **34**, 427; Mylius, *Ber.* 1903, **36**, 638; Wempe, *Zeit. anorg. Chem.*, 1912, **78**, 298; Barbieri, *Atti R. Accad. Lincei*, 1919, [5], **28**, i. 390; Posternak, *loc. cit.*

Lead Molybdate, $PbMoO_4$, occurs native as wulfenite in orange-red, transparent, tetragonal tablets and octahedra, which have a specific gravity varying from 6 to 7. When one part of sodium molybdate is fused with six parts of lead chloride and four of sodium chloride in a closed crucible, bright yellow, translucent pyramids or tablets of the artificial compound are obtained, which have a specific gravity of 6·811. If a solution of a molybdate be added to one of lead nitrate the same compound is obtained in the form of a white precipitate of high melting point. The only other lead molybdate known[1] has the formula Pb_2MoO_5.

Molybdenum Molybdates.—When molybdic acid is reduced in solution by hydrogen sulphide, sulphur dioxide, stannous chloride, zinc,[2] alcohol,[3] etc., a blue solution is obtained, and this reaction forms one of the most characteristic tests for molybdenum. This is due to the formation of an oxide or oxides intermediate between the di- and the tri-oxide, and the solutions deposit a blue precipitate of this oxide which contains water and is termed *molybdenum blue*. It may also be obtained by adding a cold dilute hydrochloric acid solution of molybdenum dioxide to one of ammonium molybdate, and in several other ways. The solubility in water of the blue oxide varies with the conditions of precipitation. It is colloidal in nature, and behaves as a negative colloid.

Much doubt exists as to the composition of this oxide; Rammelsberg assigned to it the formula $Mo_2O_5 = MoO_2,MoO_3$, and others have regarded it as $Mo_3O_8 = MoO_2,2MoO_3$, whilst according to Guichard[4] it has the composition $Mo_5O_{14},6H_2O = MoO_2,4MoO_3,6H_2O$. On the other hand, Klason[5] states that more than one compound exists, and regards these as complex derivatives of an oxide, Mo_2O_5, and molybdic acid, analogous to phosphomolybdic acid. Junius[6] has obtained it at the cathode by the electrolysis of molybdic acid in strong hydrochloric acid, and gives to it the formula, Mo_7O_{20}. The composition of the single individual compound—if, indeed, the substance is such—is known only approximately; it is possible therefore to ascribe to it various formulæ in which it may be regarded as a simple or complex molybdate of molybdenum or of the molybdenyl radicle.

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[1] Jaeger and Germs, *Zeit. anorg. Chem.*, 1921, **119**, 145. See, however, Dittler, *Zeit. Kryst. Min.*, 1913, **53**, 158; 1914, **54**, 332.

[2] Scott, *J. Ind. Eng. Chem.*, 1920, **12**, 578.

[3] Benrath, *Zeit. wiss. Photochem.*, 1917, **16**, 253.

[4] *Compt. rend.*, 1899, **129**, 722; Rogers and Mitchell, *J. Amer. Chem. Soc.*, 1900, **22**, 350; Junius, *Zeit. anorg. Chem.*, 1905, **46**, 428.

[5] *Ber.*, 1901, **34**, 148. See also Bailhache, *Compt. rend.*, 1901, **133**, 1210.

[6] *Zeit. anorg. Chem.*, 1905, **46**, 428.

Several crystalline ammoniacal double molybdates have been described[1] of the general formula $M^{I}_2M^{II}(MoO_4)_2,2NH_3$, where $M^{I} = K$ or NH_4, and $M^{II} = Cu$, Zn, Cd, Ni, or Co.

Molybdates exhibit catalytic activity in several interesting ways, *e.g.*, in influencing the oxidation of thiosulphates by hydrogen peroxide to sulphates instead of, as normally, to tetrathionates.[2]

487 *Phosphomolybdic Acid*, $P_2O_5,24MoO_3,63H_2O$ or $H_7[P(Mo_2O_7)_6],28H_2O$.—This yellow complex acid is obtained by the repeated treatment of the ammonium salt with small quantities of aqua regia, and crystallises out on evaporation of the combined solutions. It forms also crystalline hydrates containing $22H_2O$ and $12H_2O$.

The composition of these bodies has been investigated by Rosenheim and others.[3] In common with a number of other complex acids, such as those containing molybdic acid in association with silicic, oxalic, formic, arsenic, sulphurous, etc., acids, they are classed as "*heteropoly-acids*," the complex anion being composed of several anionogen radicles, of which at least one differs from the remainder.[4] Such compounds are subject to certain types of isomerism, as have already been described in the case of the chromiammines.

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[1] Briggs, *Journ. Chem. Soc.*, 1904, **85**, 672.

[2] Abel, *Zeit. Elektrochem.*, 1912, **18**, 705; Abel and Baum, *Monatsh.*, 1913, **34**, 425, 821. See also Schilow, *Zeit. physikal Chem.*, 1898, **27**, 513; Brode, *ibid.*, 1901, **37**, 299; Titoff, *ibid.*, 1903, **45**, 641; Milbauer, *ibid.*, 1907, **57**, 649.

[3] See Abegg, *Handbuch der anorganischen Chemie*, IV, [1], ii; also Friedheim, *Zeit. anorg. Chem.*, 1893, **4**, 274; Friedheim and Meschoirer, *ibid.*, 1894, **6**, 33; Kehrmann, *ibid.*, 1894, **7**, 406; Levi and Spelta, *Gazz.*, 1903, **33**, i, 207; Miolati, *ibid.*, 1903, **33**, ii, 335; *J. pr. Chem.*, 1908 [2], **77**, 417; Rosenheim and Pinsker, *Zeit. anorg. Chem.*, 1911, **70**, 79; Rosenheim, *Zeit. Elektrochem.*, 1911, **17**, 694; Rosenheim and Traube, *Zeit. anorg. Chem.*, 1915, **91**, 96; Rosenheim and Jaenicke, *ibid.*, 1912, **77**, 239; 1917, **101**, 247; Mawrow and Nikolow, *ibid.*, 1915, **93**, 170; Rosenheim and Triantaphyllides, *Ber.*, 1915, **48**, 582; Ephraim and Herschfinkel, *Zeit. anorg. Chem.*, 1909, **65**, 233, 237; Ephraim and Brand, *ibid.*, 1910, **65**, 233.

[4] See Copaux, *Compt. rend.*, 1913, **156**, 1771; Barbieri, *Atti R. Accad. Lincei*, 1913, [5], **22**, i, 781; Rosenheim, Weinberg, and Pinsker, *Zeit. anorg. Chem.*, 1913, **84**, 217; Rosenheim and Traube, *loc. cit.*; Rosenheim and Schwer, *ibid.*, 1914, **89**, 224.

The phosphomolybdic acids and their derivatives fall into two main groups: (*a*) the more complex compounds, of a yellow colour, are derivatives of the anions $[PO_4]^{VII}$ and $[Mo_2O_7]^{II}$, (*b*) the less complex compounds, colourless, are derivatives of the anions $[PO_4]^{III}$ and $[MoO_4]^{II}$. The yellow compound already mentioned belongs to the first class. A solution of this substance on long keeping undergoes hydrolysis, resulting in the production of a complex phosphomolybdic acid of the formula $H_{12}[P_2O_3(Mo_2O_7)_9]24$ to $30H_2O$. Further hydrolysis of salts of this acid yields salts of an unstable acid containing the anion $[P_4O_4(Mo_2O_7)_{17}]^{XXII}$.

If the yellow phosphomolybdates are treated with alkalis, *e.g.*, ammonia solution, white salts of the second class are obtained; the latter can also be produced directly from suitable proportions of their components, but no free acid corresponding to this group of salts has yet been prepared.

Ammonium Phosphomolybdate, $(NH_4)_3PO_4,12MoO_3$.—This salt is formed as an insoluble, canary-yellow precipitate when a solution of a molybdate is mixed with ammonia, and a small quantity of phosphoric acid in nitric acid solution added, or when the free acid is added to a strongly acid solution of the ammonium salt. Pyro- and meta-phosphates do not yield this precipitate; it is formed only when they are converted into orthophosphates, and when this change takes place slowly the compound is obtained in glistening yellow crystals (Debray). It is almost insoluble in water and in dilute acids and is also insoluble in a nitric acid solution of ammonium molybdate. The presence of hydrochloric acid and chlorides, as well as of many organic acids, with the exception of acetic acid, retards the formation, whilst in presence of an excess of phosphoric acid no precipitation occurs. Phosphates are commonly estimated by this method, so that the recovery of molybdic acid from the filtrate is a matter worthy of attention.[1] It is usually effected by precipitation with sodium phosphate, solution of the precipitate in ammonia, and removal of the phosphoric acid with magnesium salts. The molybdenum may, however, be recovered as sulphide.

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[1] See Brown, *J. Ind. Eng. Chem.*, 1915, **7**, 213; Armstrong, *ibid.*, 1915, **7**, 764; Kinder, *Stahl u. Eisen*, 1916, **36**, 1094; Rudnick and Cooke, *J. Ind. Eng. Chem.*, 1917, **9**, 109; Lehner and Schultz, *ibid.*, 1917, **9**, 684; Lynas, *Chem. Met. Eng.* 1918, 169; Neubauer and Wolferts, *Zeit. anal. Chem.*, 1919, **58**, 445; Malowan, *Chem. Zeit.*, 1918, **42**, 410.

When dried above 130°, the salt always has the composition given above, in which the ratio P_2O_5 : MoO_3 is 1 : 24, but according to Gibbs the hydrated precipitate has the composition $(NH_4)_3PO_4,12MoO_3,(NH_4)_2HPO_4,11MoO_3,8H_2O$; it is commonly, however, regarded as $(NH_4)_3PO_4,12MoO_3,2HNO_3,H_2O$. It dissolves in 10,000 parts of distilled water, in 6,600 parts of one per cent. nitric acid, and in 550 parts of hydrochloric acid of specific gravity 1·12. It is readily soluble in alkalis, and on allowing the ammoniacal solution to stand, glistening needles or prisms having the composition $2(NH_4)_3PO_4,5MoO_3,7H_2O$ separate. These are sparingly soluble in cold, readily in hot water, forming a slightly acid liquid.

Phosphomolybdic acid also precipitates strongly acid solutions of the salts of rubidium, cæsium, thallium, and the organic alkaloids, but not solutions of sodium or lithium salts. The heavy metals are also not precipitated if a sufficient amount of free acid be present. This acid is used as a reagent for the alkaloids or, in place of this, a liquid prepared by saturating a solution of sodium carbonate with molybdenum trioxide, and adding one part of sodium phosphate to every part of the trioxide, may be employed; this solution is evaporated to dryness, the residue fused, dissolved in water, filtered, and nitric acid added until the liquid becomes yellow.

Complex Arsenomolybdic acids likewise exist.

Permolybdic Acid.—The molybdates when treated with hydrogen peroxide in acid solution give a yellow coloration, but the yellow substance cannot be extracted with ether. If molybdenum trioxide be treated with hydrogen peroxide on the water-bath, and the mixture evaporated under diminished pressure, *permolybdic* or *ozomolybdic acid*,[1] H_2MoO_5,nH_2O, is obtained as an orange-red, amorphous substance. Potassium trimolybdate dissolves in hydrogen peroxide, yielding an orange-yellow solution, which on concentration at a moderate heat yields yellow crystals of *potassium permolybdate*; this, according to Muthmann and Nagel,[2] has the composition $K_2O,2MoO_3,MoO_4,3H_2O$. These chemists have shown that the molybdates of the alkali metals, when dissolved in hydrogen peroxide, can take up more oxygen to the extent of one atom or less per atom of molybdenum; in this way they have prepared a number of *permolybdates*, which readily lose oxygen on heating.

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[1] Muthmann and Nagel, *Ber.*, 1898, **31**, 1836.

[2] *Zeit. anorg. Chem.*, 1898, **17**, 73. Compare Péchard, *Compt. rend.*, 1891, **112**, 720.

A compound, K_2O_2,MoO_3,H_2O_2, is formed by the action of hydrogen peroxide at −2° on a solution of potassium permolybdate containing potassium hydroxide, followed by alcohol at −12°. This is a brick-red mass which explodes spontaneously when preserved in quantity, and loses oxygen on exposure to the air, or on treatment with water.[1]

There are also known both red and black *perthiomolybdates* of the composition $RMoS_5$ and $RMoS_6$ respectively, and *oxyfluoropermolybdates, e.g.*, $K_2[F_4MoO(O_2)],H_2O$.

MOLYBDENUM AND THE HALOGENS.

488 Normal salts of bivalent molybdenum are unknown; corresponding polymolecular complexes exist, but these do not yield the simple doubly-charged molybdenum ion.

Molybdenum Dichloride, Mo_3Cl_6, is prepared by heating the trichloride in a current of dry carbon dioxide:

$$2MoCl_3 = MoCl_2 + MoCl_4.$$

The tetrachloride volatilises, leaving the dichloride as a sulphur-yellow, amorphous powder, which does not alter in the air, and does not dissolve in water but is soluble in alcohol or ether, separating from these solutions in the amorphous condition.[2] The dichloride is conveniently obtained[3] by passing carbonyl chloride over powdered molybdenum at 700–800°, when a small quantity of the pentachloride sublimes, and the metal gradually becomes coated with a heavy, protective layer of the dichloride, which is removed by extracting it with concentrated hydrochloric acid. It is also produced when chlorine, mixed with a large excess of carbon dioxide, is passed over gently heated molybdenum in absence of oxygen.[4] It is soluble in the hydracids, in hot sulphuric acid, and in the alkalis, yielding compounds which must be regarded as salts of the radicle (Mo_3Cl_4). Thus the hydrate, $[Mo_3Cl_4]Cl_2,3H_2O$, crystallises from the hydrochloric acid solution, on keeping, in pale-yellow plates insoluble in water, but when the solution is evaporated long prisms having the formula $Mo_3Cl_6,HCl,4H_2O$, are deposited. Similarly, the solutions in alkalis contain compounds of the type $[Mo_3Cl_4](OH)_2$. The molecular weight of the dichloride in alcohol corresponds to the formula Mo_3Cl_6.[1]

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[1] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 632.

[2] Liechti and Kempe, *Annalen*, 1873, **169**, 351.

[3] Lindner and others, *Ber.*, 1922, **55**, [*B*], 1458.

[4] Blomstrand, *J. pr. Chem.*, 1859, **77**, 96; Wolf, *Chem. Zentr.*, 1918, i, 608; Lindner and others, *loc. cit.*

Molybdenum Dibromide, Mo_3Br_6, is formed by the decomposition of the tribromide by heat. It is a yellowish-red, infusible mass which does not dissolve in water or in acids.

Molybdenum Di-iodide, MoI_2, or Mo_3I_6 (?), is formed by heating the pentachloride in a current of hydrogen iodide. It is a brown, amorphous substance of density 4·3, and is insoluble in water.[2]

Chloromolybdic Hydroxide, $[Mo_3Cl_4](OH)_2,2H_2O$, precipitated by acetic acid from a solution of the dichloride in alkali, possesses amphoteric properties, and forms well-defined salts with acids.[3]

Chloromolybdic Bromide, $Mo_3Cl_4Br_2,3H_2O$, is obtained by heating the hydroxide or the chloride with hydrobromic acid. It crystallises on cooling in glistening reddish-yellow plates which scarcely dissolve in water or in dilute hydrochloric acid. Hydriodic acid forms a corresponding compound.

Bromomolybdic Hydroxide, $Mo_3Br_4(OH)_2,8H_2O$.—When molybdenum dibromide is dissolved in dilute alkali and the solution allowed to remain exposed to the air, or when ammonium chloride is added to the hot solution, the above compound is deposited in the form of golden-yellow, glistening rhombohedra closely approximating in form to the cube. These lose six molecules of water on drying over sulphuric acid, and assume a dark red colour. At 100° they lose all their water, a fine red powder remaining behind.[4]

Bromomolybdic Fluoride, $Mo_3Br_4F_2,3H_2O$, is prepared with hydrofluoric acid in the same way as the chloride, which it closely resembles.

Bromomolybdic Chloride, $Mo_3Br_4Cl_2,3H_2O$, is obtained as a pale-yellow powder on adding an excess of hydrochloric acid to the alkaline solution of the hydroxide.

Bromomolybdic Sulphate, $Mo_3Br_4SO_4,3H_2O$, can be obtained in the same way in the form of a yellow precipitate, whilst when the solution of the hydroxide is treated with ammonium molybdate and acetic acid, *bromomolybdic molybdate*, $Mo_3Br_4MoO_4,2H_2O$, is thrown down as a reddish-yellow precipitate.

Molybdenum Trifluoride has not been isolated, except in the form of double salts, but it is known to exist in solutions of molybdenum trihydroxide in hydrofluoric acid.

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[1] Muthmann and Nagel, *Ber.*, 1908, **31**, 2009. See also Koppel, *Zeit. anorg. Chem.*, 1912, **77**, 289.

[2] Guichard, *Compt. rend.*, 1896, **123**, 821.

[3] Blomstrand, *J. pr. Chem.*, 1859, 77, 100.

[4] Atterberg, *Ber.*, 1873, **6**, 1464.

Molybdenum Trichloride, $MoCl_3$, is formed when the pure pentachloride is volatilised in a current of carbon dioxide, the tube being heated strongly at one point only. The trichloride is deposited as a copper-red, crystalline crust.[1] If the pentachloride is heated in a current of hydrogen to 250° the trichloride is obtained in a form closely resembling red phosphorus.[2] The trichloride is the main product of the reaction of carbonyl chloride and molybdenum at about 600°.[3] Heated in the air it forms a white, woolly sublimate, whilst impure dichloride remains behind. It is insoluble in cold water and is decomposed by boiling water. It likewise does not dissolve in hydrochloric acid, though it is easily soluble in hot nitric acid, whilst sulphuric acid dissolves it, forming a blue solution which on heating becomes green. If the hydroxide is dissolved in hydrochloric acid a brown liquid is obtained which on evaporation dries to a black, pitch-like mass. By interaction with ammonia, a series of amido-compounds is obtained.

Molybdenum Tribromide, $MoBr_3$, is formed by the action of bromine vapour on the heated metal; it can also be prepared electrolytically.[4] It sublimes as a mass of fine blackish-green needles which are insoluble in water though soluble in cold dilute nitric, and in boiling hydrochloric, acids. On boiling with alkalis the hydroxide is formed (Blomstrand).

Molybdenum Tetrachloride, $MoCl_4$, is obtained together with the dichloride, as has been stated, by heating the trichloride in an atmosphere of carbon dioxide. The tetrachloride volatilises as a dark yellow vapour which condenses to a brown, crystalline powder. A better method[5] is to heat the dioxide with a solution of chlorine in carbon tetrachloride at 250°. When heated in moist air it is decomposed. It reacts readily with water, but is incompletely dissolved. It is only slowly soluble in hydrochloric acid, and dissolves in concentrated sulphuric acid, giving a bluish-green colour.

Molybdenum Tetrabromide, $MoBr_4$, is formed in small quantities in the preparation of the tribromide as black, glistening needles, which fuse when heated, volatilising in brownish-red vapours. These readily decompose into bromine and dibromide. In presence of air the compound deliquesces, forming a dark liquid giving with more water a yellowish-brown solution.

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[1] Blomstrand, *J. pr. Chem.*, 1859, 77, 96.

[2] Liechti and Kempe, *Ann.*, 1873, **169**, 344; Wolf, *Chem. Zentr.*, 1918, i, 608.

[3] Lindner and others, *Ber.*, 1922, **55**, [*B*], 1458.

[4] Rosenheim and Braun, *Zeit. anorg. Chem.*, 1905, **46**, 311.

[5] Michael and Murphy, *Amer. Chem. J.*, 1910, **44**, 365.

Molybdenum Tetriodide, MoI_4.—Liquid hydrogen iodide and molybdenum pentachloride yield black, insoluble crystals, probably of this compound. Double salts have also been described.[1]

Molybdenum Pentachloride, $MoCl_5$.—This, the highest chloride of molybdenum, is formed[2] by heating molybdenum or molybdenite in dry chlorine for some time, when bright, metallic, glistening, black crystals are formed which melt at 194° and boil at 268°, giving a dark red vapour with a density of 9·4–9·53,[3] corresponding to the above formula. The compound fumes on exposure to moist air, giving MoO_2Cl_2, and becomes coloured bluish-green, gradually deliquescing to a brown liquid which on dilution with water becomes colourless. Absolute alcohol, ether, and certain other solvents[4] yield green solutions, whilst chloroform, carbon disulphide, and nitrobenzene are examples of solvents yielding red-brown solutions, which differ physically from the former; the chloride also dissolves in hydrochloric acid with evolution of heat. It is decomposed by water with formation of the tetrachloride, molybdic acid, and hydrochloric acid,[5] $MoOCl_3$ probably being formed intermediately.

When molybdenum trioxide is heated with phosphorus pentachloride to 170°, the compound $MoCl_5,POCl_3$ is formed. It crystallises in dark green prisms, and when further heated decomposes into its two constituents.

Molybdenum Hexafluoride, MoF_6, is obtained by passing dry fluorine over powdered molybdenum at 60–70°, the product being collected in a receiver cooled by a mixture of solid carbon dioxide and alcohol, and then purified by distillation. It is a snow-white, crystalline substance, melting at 17° to a colourless liquid, which boils at 35°, and is decomposed by water with formation of a blue oxide.[6] It is not acted upon by chlorine, but reacts with arsenic trichloride and antimony pentachloride; it is reduced and turned blue by organic compounds.

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[1] Guichard, *Ann. Chim. Phys.*, 1901, [7], **23**, 498; Rosenheim and Koss, *Zeit. anorg. Chem.*, 1906, **49**, 148.

[2] Lindner and others, *Ber.*, 1922, **55**, [*B*], 1458.

[3] Debray, *Compt. rend.*, 1868, **66**, 732.

[4] Lloyd, *J. Physical Chem.*, 1913, **17**, 592.

[5] Guichard, *Bull. Soc. chim.*, 1901, [3], **25**, 188.

[6] Ruff and Eisner, *Ber.*, 1907, **40**, 2926.

OXY-HALIDE DERIVATIVES OF MOLYBDENUM.

489 No oxyfluoride or oxychloride containing quinquevalent molybdenum is known with certainty to exist, although a considerable number of double salts, *e.g.*, $MoOF_3,2KF,H_2O$ and $K_2(MoOCl_5),2H_2O$, have been prepared. The former class are blue or green, and the latter green, crystalline substances. The hydroxybromide, $MoO(OH)Br_2,1{\cdot}5H_2O$ yields double salts of the types $K(MoOBr_4),2H_2O$ and $K_2(MoOBr_5)$.

Sexavalent molybdenum forms a large number of derivatives containing oxygen and the halogens, many of which are volatile and crystalline, and yield crystalline double salts with other metallic halides.

Molybdenyl Tetrafluoride, $MoOF_4$, is formed by the action of anhydrous liquid hydrofluoric acid on the corresponding oxychloride as a white, hygroscopic body, melting at 97° and boiling at 180°.[1] It forms a double salt with potassium fluoride.[2]

Molybdenum Dioxydifluoride, MoO_2F_2, is obtained by heating the trioxide with cryolite or lead fluoride as an amorphous sublimate having a bluish tinge, which decomposes in the air into hydrogen fluoride and molybdenum trioxide;[3] it is obtained in solution by dissolving the trioxide in hydrofluoric acid. It may also be obtained by the action of anhydrous liquid hydrofluoric acid on the dioxydichloride as a white, hygroscopic mass, which sublimes at about 270°, and turns blue in the air.[4] Crystalline double salts are formed by dissolving the normal and polymolybdates in hydrofluoric acid; thus *potassium molybdenum oxyfluoride*, $K_2MoO_2F_4,H_2O = MoO_2F_2,2KF,H_2O$, forms lustrous plates or scales, and is soluble in water.

Molybdenyl Tetrachloride, $MoOCl_4$, has been stated to be formed by the action of chlorine on a moderately-heated mixture of carbon and molybdenum dioxide. There is formed a dark green, crystalline mass, or, if obtained at a higher temperature, light-green plates having a metallic lustre. It is readily decomposed by water, deliquescing in moist air to a blue liquid, and this on addition of water gives a blue precipitate which becomes brown in presence of ammonia. It is probable, however, that it is not an individual compound, but a mixture of the pentachloride and dioxydichloride.[1]

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[1] Ruff and Eisner, *Ber.*, 1907, **40**, 2931.

[2] Marchetti, *Zeit. anorg. Chem.*, 1895, **10**, 66.

[3] Schultze, *J. pr. Chem.*, 1880, **21**, 442.

[4] Ruff and Eisner, *Ber.*, 1907, **40**, 2933.

Molybdenum Dioxydichloride, MoO_2Cl_2.—This compound was originally supposed to be the hexachloride, its true composition being first ascertained by Rose. It is obtained by heating the dioxide in chlorine, and also, together with other chlorides, when a mixture of the trioxide and carbon is substituted for the dioxide. It sublimes usually as an amorphous mass, and melts only in closed vessels, in which it may be sublimed at low temperatures yielding thin tetragonal plates, or mossy aggregates. It dissolves readily in water and alcohol.

The *oxychloride*, $Mo_2O_3Cl_6$, is obtained by the repeated sublimation of the "oxytetrachloride," and forms well-developed violet prisms, which are decomposed on heating in the air into molybdenum dioxydichloride and chlorine. When heated to a temperature somewhat higher than that needed for its formation, it yields $Mo_3O_5Cl_8$, which forms pale red needles and is stable in the air. Oxychlorides having the composition $Mo_2O_3Cl_5$, $Mo_2O_3Cl_4$, and $Mo_3O_2Cl_7$ have also been described.[2]

Molybdenyl Dihydroxydichloride, $MoO(OH)_2Cl_2$, is obtained by the action of hydrogen chloride on the trioxide at 150–200°, and is a white, crystalline substance which is volatile without decomposition only in an atmosphere of hydrogen chloride.[3]

A number of salts of chloromolybdic acids, which may be regarded as molybdates in which the oxygen and the hydroxyl groups are partially replaced by chlorine, have been described. The acid, $MoOCl_3{\cdot}OH,7H_2O$, is obtained by the action of fuming hydrochloric acid on molybdenyl hydroxide, and a number of its salts have been prepared.[4]

Molybdenum Dioxydibromide, MoO_2Br_2, is formed when bromine vapour is passed over the heated dioxide, or when a mixture of molybdenum trioxide and boron trioxide is heated with potassium bromide:

$$MoO_3 + B_2O_3 + 2KBr = MoO_2Br_2 + 2KBO_2.$$

It forms yellow tablets which deliquesce on exposure to air.

A hydroxybromide of the composition $Mo(OH)_3Br_3$ exists.

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[1] See also Klason, *Ber.*, 1901, **34**, 148.

[2] *Annalen*, 1880, **201**, 123.

[3] Debray, *Compt. rend.*, 1858, **46**, 1101.

[4] Weinland and Knöll, *Ber.*, 1904, **37**, 569; *Zeit anorg. Chem.*, 1905, **44**, 81.

A number of bromomolybdates have been described (Weinland and Knöll).

MOLYBDENUM AND SULPHUR.

490 *Molybdenum Sesquisulphide*, Mo_2S_3, is obtained when the disulphide is heated in the electric furnace. It forms steel-grey needles of density 5·9 at 15°, and is converted into metallic molybdenum when heated to a higher temperature than that at which it is formed.[1]

Molybdenum Disulphide, MoS_2, is found native as molybdenite in Sweden, Norway, Bohemia, Saxony, the Urals, at Caldbeck Fells in Cumberland, in Connecticut, California, and elsewhere. It commonly occurs in foliated masses or in scales, and sometimes in tabular hexagonal prisms, and in its general appearance is very similar to graphite, since it possesses a metallic lustre and pure lead-grey colour, and leaves a grey trace on paper. It possesses interesting electrical properties, and between ordinary temperatures and a red heat it exists in two distinct states.[2] Molybdenite generally occurs embedded in or disseminated through granite, gneiss, zircon-syenite, granular limestone, and other crystalline rocks.

When the trioxide is fused with sulphur, or heated in a current of hydrogen sulphide, the same compound is obtained in the form of a glistening black, powder, easily distinguished from graphite by the facts that when heated before the blowpipe it is incombustible, that it oxidises when heated in the air with evolution of sulphur dioxide and formation of molybdenum trioxide, and that it is readily oxidised by nitric acid and aqua regia.

Dimolybdenum Pentasulphide, $Mo_2S_5,3H_2O$, is produced when a solution of ammonium molybdate containing sulphuric acid is reduced with zinc, the liquid filtered and treated with hydrogen sulphide. It is a brownish-black precipitate which on careful dehydration in a stream of carbon dioxide yields black Mo_2S_5. It is soluble in alkali sulphide to red solutions.[3]

Molybdenum Trisulphide, MoS_3, is formed when hydrogen sulphide is passed into the concentrated solution of a molybdate and hydrochloric acid is added to the liquid. It may likewise be prepared by boiling the molybdate of an alkali metal for a short time with ammonium sulphide, and then precipitating with dilute sulphuric acid. Thus obtained, it is a reddish-brown precipitate which dries to a blackish-brown powder. On heating in absence of air, it splits up into the disulphide and sulphur. With basic sulphides it forms soluble thio-salts.

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[1] Guichard, *Bull. Soc. chim.*, 1900, [3], **23**, 147.

[2] Waterman, *Phil. Mag.*, 1917, [6], **33**, 225. [3] Krüss, *Annalen*, 1884, **225**, 1.

Potassium Thiomolybdate, K_2MoS_4, is formed when potassium molybdate is saturated with hydrogen sulphide in presence of potassium hydroxide. On evaporating the solution, the compound crystallises out in ruby-red four- or eight-sided tablets which have a green, metallic lustre, and dissolve in water to form a yellowish-red solution.

Ammonium Thiomolybdate, $(NH_4)_2MoS_4$, is obtained by dissolving the trisulphide in ammonium sulphide, and crystallises in cinnabar-red scales.

A series of mono- and di-thiomolybdates has been described by Krüss.

Molybdenum Tetrasulphide, MoS_4, is obtained by heating pentathiomolybdic acid to 140° as a cinnamon-brown powder which undergoes slight oxidation in the air. The pentathio-acid is obtained as a reddish-brown powder by the action of dilute hydrochloric acid on the potassium salt.

Potassium Pentathiomolybdate, $KHMoS_5$, is obtained[1] by evaporating a solution of potassium dimolybdate which has been saturated with hydrogen sulphide, and separates in sparingly soluble, blood-red prisms probably belonging to the rhombic system. A black powder consisting of molybdenum di- and trisulphides separates out at the same time.[2]

Perthiomolybdic Acid, $HMoS_6$.—When a solution of normal ammonium thiomolybdate is mixed with a solution of ammonium polysulphides, *ammonium hexathiomolybdate* or *perthiomolybdate* separates out in black, lustrous needles, which are sparingly soluble in water or alcohol. By the action of caustic potash it yields the potassium salt, $KMoS_6$, which crystallises in thin, dark-brown plates, more soluble in water than the ammonium salt. The free acid, $HMoS_6$, is obtained by treating the ammonium salt with cold 10 per cent. hydrochloric acid and washing the product with carbon disulphide.[3]

Sulphomolybdic Acid, $H_2[MoO(SO_4)_2(MoO_4)]$, has also been prepared.[4]

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[1] Krüss, *Ann.*, 1884, **225**, 1. Hofmann, *Zeit. anorg. Chem.*, 1896, **12**, 55, ascribes the formula $KMoS_6$ to this compound.

[2] Krüss, *loc. cit.*

[3] Hofmann, *loc. cit.*

[4] Meyer and Stateczny, *Zeit. anorg. Chem.* 1922, **122**, 1.

MOLYBDENUM AND NITROGEN, PHOSPHORUS, BORON, CARBON AND SILICON.

491 *Molybdenum Nitride.*—When molybdenum oxide hydroxide, or mixtures of the two are heated to 500–600° with equal parts of nitrogen and hydrogen under a pressure of abou 60 atmospheres a molybdenum nitride is formed. Direct interaction, with formation of a nitride, takes place at high temperatures between molybdenum and nitrogen.[1] It is also the fina product when molybdenum trichloride or pentachloride is heated in a stream of ammonia. When heated in hydrogen or water-vapour, Mo_3N_2 yields pure metallic molybdenum and ammonia;[2] its technical application as a catalyst for the union of nitrogen and hydrogen has been the subject of investigation.

Molybdenum Phosphide, MoP, is obtained by strongly heating molybdenum trioxide and metaphosphoric acid in a carbon crucible. It forms a grey, vesicular mass having a metallic lustre and containing crystals in the cavities. On ignition in the air, it oxidises slowly, and it takes fire when dropped into fused potassium nitrate.

Molybdenum Metaphosphate, $Mo(PO_3)_3$, is formed when a solution of molybdenum trioxide in metaphosphoric acid is reduced with hydrogen at a red heat.[3]

Molybdenum Boride, probably Mo_2B, has been prepared by an arc method.

Molybdenum Carbides.—The carbide, MoC, is obtained by fusing in the electric furnace[4] a mixture of molybdenum, carbon, and aluminium, as a grey, crystalline powder of density 8·40 at 20°, whilst the compound, Mo_2C, is formed when calcium carbide is heated in the electric furnace with molybdenum dioxide.[5] The *carbonyl,* $Mo(CO)_6$, or more probably[6] $Mo_5(CO)_{26}$, is known.

Molybdenum Cyanides and Thiocyanates.—Tervalent molybdenum forms a series of complex molybdo-thiocyanates of the type $K_3Mo(CNS)_6,4H_2O$; quadrivalent molybdenum forms three distinct series of complex cyanides[7]; quinquevalent molybdenum forms double hydroxythiocyanates of the form $Mo(OH)_2(CNS)_3·Py_2$ as well as complex oxalo-derivatives.

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[1] Lederer, 1911; Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 167.

[2] D.R.-P., 246554; Austr. Pat. 62524.

[3] Colani, *Compt. rend.*, 1914, **158**, 499, 794; *ibid.*, 1917, **165**, 185.

[4] Moissan and Hoffmann, *Compt. rend.*, 1904, **138**, 1558.

[5] Moissan, *Compt. rend.*, 1897, **125**, 839. See also Hilpert and Ornstein, *Ber.*, 1913, **46**, 1669.

[6] Mond and Wallis, *J. Chem. Soc.*, 1922, **121**, 29.

[7] See a review by Collenburg, *Zeit. anorg. Chem.* 1922, **121**, 298.

Molybdenum Silicide, Mo_2Si_3, is formed as a crystalline compound when the oxide obtained by calcining ammonium molybdate is heated with silicon in the electric furnace.[1] Silicides of the formulæ MoSi and $MoSi_2$ have also been described.[2]

DETECTION AND ESTIMATION OF MOLYBDENUM.

492 Probably the most delicate qualitative test for molybdenum compounds consists in their reduction by means of stannous chloride or zinc, in the presence of a soluble thiocyanate; a blood-red coloration, due to the formation of moybdenum thiocyanate which is soluble in ether, indicates the presence of as little as 1 part in 6 millions.[3] Formation of a plum-coloured compound, $MoO_3(OEt·CSSH)_2$, with xanthic acid is another sensitive reaction,[4] as also is that of red ammonium permolybdate by means of hydrogen peroxide.[5] Acidified solutions of molybdates, when brought into contact with zinc or other suitable reducing agents, become blue, then green, and finally brown; hydrazine, iodides, or quinol give a blue colour, whilst catechol yields an orange solution.[6] Reduction is effected by sulphurous acid only if the solutions are neutral or but slightly acid. When a trace of a molybdenum compound is evaporated nearly to dryness with a few drops of sulphuric acid, a blue colour develops. This reaction also is very sensitive.

Molybdenum trisulphide is slowly precipitated from an acid solution of a molybdate by hydrogen sulphide, which first causes the development of a blue colour. The precipitate dissolves readily in ammonium sulphide solution, yielding ammonium thiomolybdate which on acidification again deposits the brown trisulphide.

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[1] Vigouroux, *Compt. rend.*, 1899, **129**, 1238.

[2] Hönigschmid, *Monatsh.*, 1907, **28**, 1017; Watts, *Chem. Zentr.*, 1908, i, 598; Wedekind, D.R.-P. 294267.

[3] Browning, *Amer. J. Sci.*, 1915, [4], **40**, 349; Moir, *J. Chem. Metall. Min. Soc. S. Africa*, 1916, **16**, 191; Stěrba-Böhm and Vostrěbal, *Zeit. anorg. Chem.*, 1920, **110**, 81.

[4] Koppel, *Chem. Zeit.*, 1919, **43**, 777; Malowan, *Zeit. anorg. Chem.*, 1919, **108**, 73.

[5] Komarowsky, *Chem. Zeit.*, 1913, **37**, 957.

[6] Moir, *loc. cit.* See also Kafka, *Zeit. anal. Chem.*, 1912, **51**, 482; Pozzi-Escot, *Bull. Soc. chim.*, 1913, [4], **13**, 402, 1042.

Fuchs,[1] describes a test for molybdenite whereby the mineral is dissolved in fused potassium hydroxide, yielding a red double sulphide; if this is dissolved in water, a series of colour changes, through blue, green, and yellow, takes place.

A solution of ammonium molybdate in nitric acid becomes yellow-coloured on the addition of a few drops of sodium phosphate solution, and on keeping or warming a heavy yellow precipitate of ammonium phosphomolybdate[2] separates out.

Molybdenum compounds impart to a bead of microcosmic salt or borax in the reducing flame a fine green colour; the bunsen flame is coloured green by molybdic acid.

For the gravimetric estimation of molybdenum, the compound is converted into a neutral molybdate which is precipitated from aqueous solution as mercurous molybdate or lead molybdate, the latter method now being almost exclusively employed.[3] In the former case, mercury is removed during ignition, and the residual molybdenum trioxide, which must not be heated to more than 425°, is weighed.[4] If the molybdenum is to be estimated by way of the sulphide,[5] the latter may be directly precipitated by hydrogen sulphide from a solution acidified preferably with formic acid, or the gas may be passed into an ammoniacal solution containing the molybdic acid, and the resulting solution of ammonium thiomolybdate decomposed with acid. In either case the sulphide is usually converted into the trioxide by roasting and treatment with nitric acid, but it may be dried in carbon dioxide and weighed as such.

It is also possible to estimate molybdenum by volatilisation of the trioxide in a current of carbon tetrachloride vapour.[6]

Molybdenum trioxide can be separated from admixture with tungsten trioxide by dissolving it in a mixture of selenium oxychloride and sulphuric acid.[7]

Volumetric methods which have been proposed include the titration of the sesqui-compounds with potassium permanganate and methods based on the reactions: $2MoO_3 + 2HI = H_2O +$

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[1] *Informaciones y mem. soc. ing. Peru*, 1918, **20**, 423.

[2] Arsonates give a precipitate of similar appearance.

[3] Raper, *Biochem. J.*, 1914, **8**, 649; Taylor and Miller, *J. Biol. Chem.*, 1915, **21**, 255; Weiser, *J. Physical Chem.*, 1916, **20**, 640.

[4] Treadwell, *Zeit. Elektrochem.*, 1913, **19**, 219; Wolf, *Zeit. angew. Chem.*, 1918, **31**, i, 140.

[5] Binder, *Chem. Zeit.*, 1918, **42**, 255; Wolf, *loc. cit.*; Stärba-Böhm and Vostřebal, *loc. cit.*

[6] Jannasch and Laubi, *J. pr. Chem.*, 1918, [2], **97**, 154.

[7] Merrill, *J. Amer. Chem. Soc.*, 1921, **43**, 2383.

$Mo_2O_5 + I_2$, and $KIO_3 + Mo_2O_3 + 2HCl = KCl + Mo_2O_5 + ICl + H_2O$.[1]

Atomic Weight of Molybdenum.—The determination of the atomic weight of molybdenum has been frequently made, but with varying results. After an inaccurate determination by Berzelius, Svanberg and Struve obtained the number 92·5, which was confirmed by Berlin, and then generally adopted. The investigation of Dumas[2] then showed that the number just quoted was distinctly too low, the average obtained by the reduction of the trioxide to the metal in a current of hydrogen being 95·9; the numbers in the different experiments varying, however, from 95·3 to 96·2. Debray[3] obtained the number 95·5 by the same method, whilst Liechti and Kempe[4] by the analysis of the di-, tri-, and penta-chlorides of molybdenum obtained the same average number as Dumas; but in this case also the numbers found in the different experiments varied considerably. Smith and Maas[5] found the number 96·06, the method adopted being to heat pure sodium molybdate in a current of hydrogen chloride:

$$Na_2MoO_4 + 4HCl = 2NaCl + Mo(OH)_2OCl_2 + H_2O.$$

The last two being volatile, only pure sodium chloride remains behind, and from the amount of this obtained from a given quantity of sodium molybdate, the above number was obtained as the average of ten closely agreeing experiments. Seubert and Pollard,[6] by the acidimetric determination of molybdic acid, obtained the number 95·92, and by the reduction of the trioxide to the metal in a current of hydrogen the number 96·01. By a determination of the ratio $Mo : MoO_3$, Vandenberghe[7] obtained the value 96·06, whilst Müller,[8] employing the same ratio, found the value 96·029. The mean value of the best determinations is 96·04 ± 0·01. The atomic weight now adopted (1922) is 96·0.[9]

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[1] Jamieson, *J. Amer. Chem. Soc.*, 1917, **39**, 246. For details of certain other methods, see Zinberg, *Zeit. anal. Chem.*, 1913, **52**, 529; Marbaker, *J. Amer. Chem. Soc.*, 1915, **37**, 86; Travers, *Compt. rend.*, 1917, **165**, 362; Hoepfner and Binder, *Chem. Zeit.*, 1918, **42**, 315, 564; Scott, *J. Ind. Eng. Chem.*, 1920, **12**, 578; Camp and Marden, *ibid.*, 1920, **12**, 998; Nakazono, *J. Chem. Soc. Japan*, 1921, **42**, 526.

[2] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.

[3] *Compt. rend.*, 1868, **66**, 732.

[4] *Annalen*, 1873, **169**, 360.

[5] *Zeit. anorg. Chem.*, 1893, **5**, 280.

[6] *Ibid.*, 1895, **8**, 434.

[7] *Mem. Acad. Belg.*, 1898, **56**.

[8] *J. Amer. Chem. Soc.*, 1915, **37**, 2046.

[9] Gerber, *Mon Sci.*, 1917, [5], **7**, 73, claims that molybdenum is not a simple substance, but is accompanied by *neo-molybdenum* of higher atomic weight.

TUNGSTEN. W = 184·0. At. No. 74.

493 The minerals tungsten or heavy-stone, now termed scheelite or calcium tungstate, and wolfram (the *lupi spuma* of Agricola) were, up to the middle of the eighteenth century, both classed among the tin ores. In 1781, Scheele proved that tungsten was composed of lime combined with a peculiar acid, and in the same year Bergmann stated that, in his opinion, this acid was a metallic calx. Two years later the Spanish chemists Juan, José, and Fausto d'Elhujar,[1] showed that this same acid is contained in the mineral wolfram, combined with iron and manganese. They also prepared metallic tungsten.

Tungsten is not a common metal, being found only in a few minerals, some of which occur, however, in fairly large quantities. The most important of these are wolfram, or wolframite, a tungstate of iron and manganese, $(Fe,Mn)WO_4$, found in Cornwall, in Cumberland, on Rona in the Hebrides, in County Wicklow, at Zinnwald, in many localities in the United States, in Burmah, and also in Austria-Hungary, Spain, Portugal, Queensland, New Zealand, Tasmania, Canada, and various parts of South America, and scheelite or calcium tungstate, $CaWO_4$. In addition to these, tungsten occurs in the following somewhat rare minerals: wolframochre, WO_3; stolzite or lead tungstate, $PbWO_4$; ferberite, $FeWO_4$, which occurs in large quantities in Colorado; hübnerite, $MnWO_4$; cuproscheelite, or cuprotungstite, $(Ca,Cu)WO_4$; chillagite,[2] $PbWO_4,PbMoO_4$, and tungstenite,[3] WS_2(?).

Metallic Tungsten is obtained from wolfram by a method which consists of three distinct stages.[4] Sodium tungstate is first prepared by heating together a mixture of the ground ore and sodium carbonate. When this operation is carried out under proper conditions the extraction is complete, and at the same time any tin and silica present are left insoluble. The sodium tungstate thus formed is dissolved in water and separated from the oxides of iron, aluminium, manganese, tin, and silicon by filtration, and tungstic acid, H_2WO_4, is then precipitated by means of acid. In this step care is necessary to prevent the formation of hydrated tungstic acid, which is soluble. The tungstic acid thus obtained is washed free from sodium salts and dried, and the resulting tungstic oxide is mixed with carbonaceous materials and submitted to a high temperature in crucibles for reduction to metal. A well-fired crucible when opened should be uniform throughout, with the exception of a thin layer of tops or undecomposed tungstic oxide and carbon, which can be readily removed.

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[1] *A Chemical Analysis of Wolfram and Examination of a New Metal, which enters into its Composition.*" Translated from the Spanish by C. Cullen, to which is prefixed a translation of Mr. Scheele's analysis of the Tungsten, or heavy-stone, with Mr. Bergmann's supplemental remarks. London, 1785.

[2] Ullmann, *J. Roy. Soc. New South Wales*, 1912, **46**, 186.

[3] Wells and Butler, *J. Washington Acad. Sci.*, 1917, **7**, 596.

[4] Hadfield, *J. Iron Steel Institute*, 1903, **64**, 38.

Tungsten containing 99 per cent. of the metal has been obtained by fusing tungsten trisulphide with lime.[1]

Metallic tungsten may be prepared on the small scale by the reduction of the trioxide with carbon or in a current of hydrogen,[2] by the reduction of the chloride in hydrogen or sodium vapour, or by heating a mixture of the trioxide with one-tenth of its weight of sugar charcoal in the electric furnace; if care be taken that complete fusion of the metal does not occur, the latter is free from carbon.[3] The metal thus obtained is as a rule fused on the surface, but is porous internally, and can be welded like iron. It has been obtained in the form of a regulus by reducing the oxide with aluminium turnings and at the close of the reaction adding aluminium foil, and blowing in a stream of oxygen, or by adding liquid air to a mixture of the oxide and aluminium and igniting as in the thermite process[4] The powdered metal can be prepared also by heating the oxide with zinc and extracting the product with caustic soda solution,[5] and by the action of dilute acids on the alloys of manganese and tungsten.[6] Electrolysis of the fused trioxide or salts, or of the latter in solution, has been found to yield metallic tungsten.

Powdered tungsten, or the massive form obtained from it by fusion (although this process is not simple, the metal attacking the receptacle at the high temperatures necessary and becoming impure) are used in the manufacture of alloys, particularly ferrotungsten. The massive form is not sufficiently ductile, nor indeed sufficiently pure, for use in the manufacture of tungsten filaments for electric incandescence lamps, so that until recently it was necessary to form the filaments of the powdered metal together with an appropriate binding material. Now,[1] however, the finely divided metal is formed into rods by pressure alone, and heated in hydrogen by slowly drawing it through a small heated coil, whereby it is converted into elongated crystals; it then responds to the mechanical treatment necessary to give malleability and ductility.

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[1] Weiss, *Zeit. anorg. Chem.*, 1910, **65**, 279.

[2] Davis, *J. Ind. Eng. Chem.*, 1919, **11**, 201.

[3] Moissan, *Compt. rend.*, 1896, **123**, 13. See also Mennicke, "Metallurgie des Wolframs," Berlin, 1911.

[4] Stavenhagen, *Ber.*, 1899, **32**, 1513, 3064.

[5] Delépine, *Compt. rend.*, 1900, **131**, 184. [6] Arrivant, *ibid.*, 1906, **143**, 594.

In the form of a regulus, tungsten has a slightly darker colour than zinc, shows a crystalline (cubic[2]) structure, is harder than glass, (its degree of hardness depends on its previous treatment, and is higher if the metal is impure); its density is above 19, but figures varying between 18·7 and 21·4 have been obtained. The metal is not magnetic, it has a mean specific heat 0·0340 between 15° and 93°, 0·0375 between 15° and 423°,[3] melts[4] at 3540° ± 30°, and can be volatilised in the electric furnace, but is more refractory than iron, molybdenum, or uranium.[5]

Tungsten has the smallest compressibility of any substance hitherto studied.[6] It occupies a place in the potential series between antimony and mercury, and exhibits passivity under certain conditions.[7] It is attacked by fluorine at the ordinary temperature with incandescence, and by chlorine at 250–300°, but has no action on nitrogen or phosphorus at a red heat; when heated with carbon, silicon, or boron in the electric furnace, it yields crystalline compounds having a metallic lustre which are hard enough to scratch rubies. It is slowly attacked by fuming sulphuric acid and by fused alkalis.[8] At a red heat, the powdered metal burns in air, forming the trioxide,[9] but it is not readily oxidised by moist air, although slowly attacked by water containing carbon dioxide[10]; it is readily oxidised when heated with oxidising agents such as lead dioxide or potassium chlorate. Sulphuric, hydrochloric, and hydrofluoric acids act upon it slowly, but it is more readily dissolved by a mixture of nitric and hydrofluoric acids; the powdered metal is rapidly oxidised by aqua regia, and dissolves in boiling potassium hydroxide solution with formation of potassium tungstate and evolution of hydrogen, whereas the fused metal is not attacked by aqua regia, but dissolves slowly in fused potash (Stavenhagen). Tungsten is utilised for the production of filaments for incandescence electric lamps which have a very high efficiency.[1] It is also largely employed in the manufacture of tungsten steels, generally in the form of ferrotungsten. In the finely-divided form, it is a valuable catalyst in Haber's process for the synthesis of ammonia.

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[1] Gross, *Jahrb. Radioaktiv. Elektronik*, 1918, **15**, 270.

[2] Debye, *Physikal. Zeit.*, 1917, **18**, 483.

[3] Defacqz and Guichard, *Ann. Chim. Phys.*, 1901, [7], **24**, 139. See also Worthing, *J. Franklin Inst.*, 1918, **185**, 707.

[4] Langmuir, *Physical Rev.*, 1915, **6**, 138.

[5] Moissan, *Compt. rend.*, 1906, **142**, 425.

[6] Richards and Bartlett, *J. Amer. Chem. Soc.*, 1915, **37**, 470.

[7] Fischer and Roderburg, *Zeit. anorg. Chem.* 1913, **81**, 170; Fischer and Rideal, *ibid.*; Koerner, *Trans. Amer. Electrochem. Soc.*, 1917, **31**, 221.

[8] Ruder, *J. Amer. Chem. Soc.*, 1912, **34**, 387.

[9] Langmuir, *J. Amer. Chem., Soc.*, 1913, **35**, 105.

[10] Wöhler and Prager, *Zeit. Elektrochem.*, 1917, **23**, 199.

Alloys.—Certain definite compounds of tungsten with other metals are believed to exist; ferrotungsten is, however, the most important.[2] Cobalt forms the alloys[3] Co_3W and CoW.

COMPOUNDS OF TUNGSTEN.

TUNGSTEN AND OXYGEN.

494 Tungsten forms two definite oxides[4]: tungsten dioxide, WO_2, and tungsten trioxide, WO_3. These combine together to form compounds analogous to the blue oxides of molybdenum.

A black gelatinous precipitate, considered to be the hydrated *sesquioxide*, W_2O_3, is formed when potassium hydroxide solution, followed by a weak acid, is added to the product of reduction of tungsten hexachloride with sodium amalgam. It is unstable, being converted into the dioxide.[5]

Tungsten Dioxide, WO_2.—This oxide is formed when a current of hydrogen is passed over the trioxide, WO_3, at a dull red heat. It may also be obtained in the wet way by reducing the trioxide, mixed with hydrochloric acid, by means of metallic zinc, or by the action of water on the tetrachloride. In preparing it in the dry way care is needed, as if the temperature be too high metallic tungsten is formed, whereas if the heat be not sufficient, the intermediate blue oxide is produced. Tungsten dioxide is a brown powder of density 12·1, which has a copper-red colour when crystalline trioxide is employed for its preparation. It is strongly pyrophoric, and must be cooled in hydrogen for some time before it is exposed to the air. It is slightly soluble in concentrated hydrochloric acid and sulphuric acid, yielding purple solutions. Oxidising agents convert it rapidly into the trioxide. It dissolves in potash to form hydrogen and potassium tungstate:

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[1] *J. für Gasbeleuchtung*, 1906, **49**, 756; *Nature*, 1907, **76**, 156; *J. Inst. Elect. Engineers*, 1907, **38**, 211; Weber "Die elektrischen Metallfadenglühlampen," Leipzig, 1914; Müller, "Metalidrahtlampe," Halle, 1914; Lummer, "Grundlagen, Ziele und Grenzen der Leuchttechnik," Berlin, 1918.

[2] Honda and Murakami, *Sci. Rep. Tohôku Imp. Univ.*, 1918, **6**, 235, state that the only compound formed in tungsten steels has the formula Fe_2W.

[3] Kreitz, *Metall u. Erz*, 1922, **19**, 137.

[4] For the thermochemistry and vapour pressures of the oxides, see van Liempt, *Zeit. anorg. Chem.*, 1921, **120**, 267.

[5] Hill, *J. Amer. Chem. Soc.*, 1916, **38**, 2383.

$$WO_2 + 2KOH = K_2WO_4 + H_2.$$

Tungsten Trioxide, WO_3.—This oxide occurs native as wolframine, a yellow powder found together with other tungsten minerals in Cumberland, near Limoges, in Connecticut, and in North Carolina. In order to prepare the trioxide, the method already described may be adopted, or finely powdered wolfram may be digested for a long time with hydrochloric acid, the mixture frequently shaken, the acid renewed, and a little nitric acid added towards the end of the process to oxidise the iron. This is continued until the acid has dissolved out the whole of the iron and manganese and the brown powder has become yellow-coloured. The insoluble portion consisting of tungsten trioxide and undecomposed wolfram and quartz, after being well washed, is shaken up with a solution of ammonia which dissolves the liberated tungstic acid. The solution is crystallised and the crystals are converted into the trioxide by ignition in the air. Wöhler converted the wolframite into calcium tungstate by fusing the finely powdered mineral for an hour with twice its weight of calcium chloride and then lixiviating, when calcium tungstate remained behind. This was then decomposed by nitric acid, and tungsten trioxide obtained by igniting the yellow precipitate formed. The native calcium tungstate (scheelite) can also be decomposed in this way.

Tungsten trioxide is a bright canary-yellow coloured, amorphous powder which becomes dark orange on heating, but regains its bright yellow colour on cooling; it melts at 1473°. A very slight admixture of sodium salt imparts to the oxide a greenish tint which no amount of oxidation can remove (Roscoe). It also becomes greenish on exposure to light.[1] Tungsten trioxide has been obtained in the crystalline state by Debray, by igniting a mixture of sodium tungstate and carbonate in a current of hydrochloric acid, when the trioxide is obtained in olive-green rectangular prisms which sublime at a white heat. The crystalline trioxide has also been prepared by heating hydrated tungstic acid with borax in a porcelain tube (Nordenskjöld). The density of tungsten trioxide is 7·2. It is insoluble in water. Reduction to the metal is effected by hydrogen or carbon, various oxides of indefinite conposition being formed intermediately.[1] The amorphous oxide is soluble and the crystalline oxide insoluble in sulphur monochloride.[2]

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[1] See van Liempt, *loc. cit.*; Burger, *Zeit. anorg. Chem.*, 1922, **121**, 240.

TUNGSTIC ACID AND THE TUNGSTATES.

495 Tungsten trioxide is an acid-forming oxide, and yields two tungstic acids, the normal acid, H_2WO_4, and metatungstic or tetratungstic acid, $H_2W_4O_{13}$, the salts of which correspond to the tetrachromates and tetramolybdates. In addition to the salts corresponding to these acids, a large number of other tungstates analogous to the polychromates and polymolybdates have been prepared, the formulæ ascribed to which are given in the following table:[3]

$M^{I}_2WO_4 = M^{I}_2O,WO_3.$

$M^{I}_2W_2O_7 = M^{I}_2O,2WO_3.$

$M^{I}_2W_3O_{10} = M^{I}_2O,3WO_3.$

$M^{I}_2W_4O_{13} = M^{I}_2O,4WO_3.$

$M^{I}_2W_5O_{16} = M^{I}_2O,5WO_3.$

$M^{I}_2W_6O_{19} = M^{I}_2O,6WO_3.$

$M^{I}_2W_8O_{25} = M^{I}_2O,8WO_3.$

$M^{I}_4W_5O_{17} = 2M^{I}_2O,5WO_3.$

$M^{I}_6W_7O_{24} = 3M^{I}_2O,7WO_3.$

$M^{I}_8W_3O_{13} = 4M^{I}_2O,3WO_3.$

$M^{I}_{10}W_{12}O_{41} = 5M^{I}_2O,12WO_3.$

Many of these crystallise with a number of molecules of water, forming well-developed crystals. The salts of the formula $M^{I}_{10}W_{12}O_{41}$ are termed paratungstates. Copaux[4] formulates the paratungstates as $R_6[H(W_2O_7)_3]$,aq., whilst Rosenheim[5] formulates them as $R_5H_5[H_2(WO_4)_6]$,aq.

The tungstates also yield complex salts with many other acidic oxides analogous to the complex molybdates.

Tungstic Acid, H_2WO_4.—When a solution of a tungstate is precipitated by an acid in the cold, a white precipitate is gradually[1] thrown down consisting of hydrated tungstic acid, H_2WO_4,H_2O.[2] This is soluble in water, possesses a bitter taste, and reddens litmus. If, on the other hand, an excess of hot acid be used, anhydrous tungstic acid, H_2WO_4, separates as a yellow powder, insoluble in water and in all acids except hydrofluoric acid. If pure tungsten hexachloride be exposed to the action of moist air, the red monoxychloride is first formed, and this soon passes into a fine flocculent mass of white tungstic acid.

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[1] Davis, *J. Ind. Eng. Chem.*, 1919, **11**, 201.

[2] Smith and Fleck, *J. Amer. Chem. Soc.*, 1899, **21**, 1008.

[3] See Schaefer, *Zeit. anorg. Chem.*, 1904, **38**, 142, where the literature is quoted. Acids containing a complex radicle composed of one kind of anionogen radicle only are termed "iso-poly-acids"; those composed of two or more different anionogen radicles are termed "hetero-poly-acids." The exact quantitative examination of these bodies is rendered difficult by the high atomic weight of tungsten; for this and other reasons there is still considerable uncertainty regarding the formulation of the complex tungstic acids.

[4] *Compt. rend.*, 1913, **156**, 1771.

[5] *Zeit. anorg. Chem.*, 1916, **96**, 139. See also Prandtl, *Ber.*, 1915, **48**, 692.

The tungstates are insoluble in water, except those of the alkali metals; and even of these, some tungstates of potassium and ammonium are only sparingly soluble. The tungstates of the alkaline-earth metals, and of the heavy metals are mostly amorphous powders, but they may be obtained crystalline by double decomposition at a high temperature.

Metatungstic Acid,

$$H_2W_4O_{13},8(?8{\cdot}5)H_2O, \textit{ i.e., } H_6H_4[H_2(W_2O_7)_6],21H_2O.$$

—The salts of this acid were discovered by Margueritte,[3] but the acid was first prepared by Scheibler.[4] For this purpose the barium salt is decomposed by dilute sulphuric acid or the lead salt with hydrogen sulphide. Metatungstic acid crystallises in small, yellow octahedra which effloresce in the air. On ignition it is converted into the trioxide. It is readily soluble in water and the solution possesses a harsh, bitter taste. When the solution is concentrated by boiling, a white hydrate is deposited and afterwards the trioxide separates. The metatungstates of the alkali metals are formed when the ordinary tungstates are boiled with tungstic acid until the filtrate gives no precipitate on addition of hydrochloric acid.[5] The metatungstates of the other metals are, as a rule, easily soluble in water, and are best prepared by double decomposition of the barium salt with the corresponding sulphate or carbonate. The warm solutions usually yield the salts in amorphous masses when evaporated, but when concentrated over sulphuric acid they frequently crystallise. The metatungstates possess a bitter taste, and are not precipitated by acids; on long boiling ordinary tungstic acid is deposited.

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[1] Lottermoser, *Kolloid Zeit.*, 1914, **15**, 145.

[2] See, however, Hüttig and Kurre, *Zeit. anorg. Chem.*, 1922, **122**, 44; also Burger, *ibid.*, 1922, **121**, 240.

[3] *Ann. Chim. Phys.*, 1846, [3], 17, 475.

[4] *J. pr. Chem.*, 1861, **83**, 310.

[5] Copaux, *Ann. Chim. Phys.*, 1909, [8], 17, 207; *Compt. rend.*, 1913, **156**, 71.

Colloidal Tungstic Acid.—This modification of tungstic acid was discovered by Graham,[1] and is obtained by dialysing a 5 per cent. solution of sodium tungstate to which sufficient hydrochloric acid has been added to combine with the sodium. The liquid remaining in the dialyser possesses a bitter, astringent taste and does not gelatinise on the addition of acids, even on boiling. On evaporating in a vacuum, a transparent, gum-like mass is obtained, and this can be heated to 200° without losing its solubility, whilst at a red heat it is transformed into tungsten trioxide, losing 2·4 per cent. of water. When moistened with water the colloidal acid becomes pasty and adhesive like gum, dissolving completely in one quarter of its weight of water. It can also be obtained by dialysing a solution of freshly precipitated tungstic acid in oxalic acid.[2] The photochemical and other behaviour of colloidal tungstic acid suggest that it exists in two forms.

Sodium Tungstates.—The *normal salt*, $Na_2WO_4,2H_2O$, is prepared like the potassium salt, and is obtained on the large scale by fusing wolfram with soda ash. It crystallises in thin, lustrous, rhombic prisms which dissolve in four parts of cold and in two parts of boiling water.[3] The solution possesses a bitter taste and has an alkaline reaction. The crystals do not undergo alteration in the air, and they are insoluble in alcohol; a decahydrate is also known. When heated to 200° the salt becomes opaque and loses its water, and fuses at 665°.

Sodium Paratungstate, $Na_{10}W_{12}O_{41},28H_2O$.—This salt, which is the one known commercially as tungstate of soda, is prepared on the large scale by roasting wolframite with soda ash and lixiviating the fused mass. The boiling solution is nearly neutralised with hydrochloric acid and allowed to crystallise at the ordinary temperature, when the salt separates in large triclinic crystals. At a higher temperature crystals containing 25 and 21 molecules of water are formed. The salt can also be prepared by electrolysis of solutions of the normal tungstate.[4] It is sometimes used in place of sodium stannate as a mordant in dyeing and calico printing, and is also employed for rendering cotton, linen, "flannelette," etc., uninflammable.[5] Rosenheim[6] formulates the compound: $Na_{10}H_4[H_4(WO_4)_6(W_2O_7)_3],24H_2O$. The anhydrous salt melts at 705·8°.

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[1] *Journ. Chem. Soc.*, 1864, **17**, 325.

[2] Pappadà, *Gazz.*, 1902, **32**, ii, 22. Compare Sabanéeff, *Zeit. anorg. Chem.*, 1897, **14**, 354. See also Wassiljewa, *Zeit. wiss. Photochem.*, 1913, **12**, 1.

[3] Marignac, *Ann. Chim. Phys.*, 1863, [3], **69**, 39.

[4] Lottermoser, *Kolloid Zeit.*, 1922, **30**, 346.

[5] Versmann, *Reports of the Juries of the Exhibition of* 1862.

[6] *Zeit. anorg. Chem.*, 1916, **96**, 139. Marignac considered that the paratungstates obtained by him were of the form $3Na_2O,7WO_3$.

Sodium Metatungstate (Tetratungstate), $Na_2W_4O_{13},10H_2O$, is formed by prolonged boiling of the normal salt with tungsten trioxide.[1] It crystallises in efflorescent octahedra probably belonging to the regular system. Cold water dissolves 10·69 times its weight of this salt; there is a rapid increase in solubility with rise of temperature. It loses its water at a red heat (Marignac and Scheibler), fusing at 706°.

Tungstates typified by the salt, $4Na_2O,10WO_3,23H_2O$ (which melts, when anhydrous, at 680·8°), have also been found to constitute a definite series.[2] The salt, $9Na_2O,22WO_3$, melts at 683·3°.

Potassium Tungstates.—The *normal salt*, K_2WO_4,[3] is obtained by adding tungsten trioxide little by little to its own weight of fused potassium carbonate. On cooling a solution of the fused mass in hot water, normal potassium tungstate crystallises in large, acicular, anhydrous crystals, or in large, prismatic crystals, $K_2WO_4,2H_2O$ (Marignac). When the normal salt is treated in aqueous solution with an acid, or when tungsten trioxide is added to its boiling solution until no more dissolves, glistening scales of the *paratungstate*, $K_{10}W_{12}O_{41},11H_2O$, are deposited; metatungstate is formed at the same time. The paratungstate dissolves more readily in hot than in cold water, and the solution has an acrid taste and acid reaction. When alcohol is added to the aqueous solution a precipitate is formed; this dissolves on warming, but, on cooling, the solution deposits scales of *potassium metatungstate*, $K_2W_4O_{13},5H_2O$; a second hydrated salt containing $8H_2O$, crystallising in octahedra, is obtained from the mother-liquor of the normal tungstate. The following compounds have also been described: $K_2O,2WO_3,2H_2O$; $2K_2O,5WO_3,4H_2O$; $K_2O,3WO_3,2H_2O$; $K_2O,8WO_3$.

Ammonium Tungstates.—The normal salt is extremely unstable.[4] When a solution of tungstic acid in ammonia is allowed to evaporate over calcium oxide, warty concretions of the salt $2(NH_4)_2O,3WO_3,3H_2O$ are sometimes deposited, which easily give off ammonia. The usual product is, however, the *paratungstate*, $5(NH_4)_2O,12WO_3,11H_2O$ [or possibly $3(NH_4)_2O,7WO_3,6H_2O$], formulated by Rosenheim as $(NH_4)_{10}H_4[H_4(WO_4)_6(W_2O_7)_3],7H_2O$. If, however, the ammoniacal solution of the trioxide be allowed to evaporate whilst warm, monoclinic crystals of $(NH_4)_{10}W_{12}O_{41},5H_2O$ separate out. When tungsten trioxide is boiled with ammonia, tetragonal prisms of *ammonium metatungstate*, $(NH_4)_2W_4O_{13},8H_2O$, *i.e.* $(NH_4)_6H_4[H_2(W_2O_7)_6],21H_2O$, are obtained. These are very soluble, and effloresce quickly on exposure to the air. A hexahydrate is also known. Besides these, many other ammonium tungstates have been prepared (Marignac), as well as compounds of these with ammonia, and ammoniacal derivatives of other tungstates.[1] Commercial ammonium tungstate is stated[2] to possess the formula $(NH_4)_4W_5O_{17},2H_2O$.

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[1] See also Lottermoser, *loc. cit.*, for an electrolytic method.

[2] Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2027.

[3] Potassium tungstate is trimorphous; see Amadori, *Atti R. Accad. Lincei*, 1914, [5], **23**, i, 800.

[4] Rosenheim and Jacobsohn, *Zeit. anorg. Chem.*, 1906, **50**, 297.

Normal Calcium Tungstate, $CaWO_4$.—This occurs native as scheelite in vitreous, yellowish-white, tetragonal pyramids. Its chief source is Australia, but it is also met with in the following localities: Zinnwald, Caldbeck Fell in Cumberland, Piedmont, Dalecarlia, in the Vosges, at Huntingdon in Connecticut, and at the Mammoth mining district in Nevada. The crystals usually contain iron, and are found in crystalline rocks in connection with tin-ore, topaz, apatite, wolfram, etc.

It is prepared artificially as a white, insoluble precipitate by mixing solutions of calcium chloride and a normal tungstate, and can be obtained in the crystalline form of scheelite by heating the precipitate mixed with lime in a current of hydrogen chloride. If a hot solution of metatungstic acid be saturated with calcium carbonate, calcium metatungstate, $CaW_4O_{13},10H_2O$, is obtained crystallising in small, tetragonal octahedra.[3]

Lead Tungstate, $PbWO_4$, occurs as stolzite at Zinnwald in Bohemia, at Bleiberg in Carinthia, in Chili, and at Southampton, Massachusetts. It crystallises in translucent, tetragonal pyramids having a density of 7·87 to 8·13.

Ferrous Tungstate, $FeWO_4$, occurs as wolfram, $(Fe,Mn)WO_4$, which contains manganese as an isomorphous constituent, in Cornwall, Cumberland, France, the Erzgebirge, and various parts of the United States. Wolfram crystallises in the monoclinic system in dark grey or brownish-black prisms having a metallic lustre and a density of 7·3.

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[1] Taylor, *J. Amer. Chem. Soc.*, 1902, **24**, 620; Briggs *Journ. Chem. Soc.* 1904, **85**, 672.

[2] Arnold, *Zeit. anorg. Chem.*, 1914, **88**, 74.

[3] See also Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 2027.

Manganese Tungstate, $MnWO_4$, is found as hübnerite in Nevada in a vein from three to four feet wide.

Chromium Tungstates.—A number of such compounds have been described, but there is little doubt that some are merely mixtures of simpler compounds.[1]

Tungsten Tungstates.—By the partial reduction of tungsten trioxide a number of oxides of tungsten have been prepared, having a composition intermediate between that of the dioxide and trioxide. These have a blue or purple-red colour, and are probably combinations of the acidic trioxide with the more basic dioxide. Thus by the action of hydrogen on the trioxide at 250° the compound $W_3O_8 = 2WO_3,WO_2$ is formed, which has a deep blue colour; the same oxide, when prepared by heating ammonium metatungstate to a red heat, has a purple-red colour and metallic reflex.[2] Other blue oxides having the compositions $W_2O_5 = WO_2,WO_3$; $W_4O_{11} = 3WO_3,WO_2$; $W_5O_{14} = 4WO_3,WO_2$ have been described; in addition, Deal has obtained oxides containing less oxygen than the dioxide, by the action of concentrated sulphuric acid on metallic tungsten under suitable conditions. It is therefore uncertain whether the blue oxide is a chemical individual or an admixture. Hydrated blue oxides are readily obtained by reduction of tungsten trioxide or tungstic acid, *e.g.*, with stannous chloride, hydrogen iodide, or alcohol.[3]

496 *Tungsten Bronzes*.—These remarkable compounds, obtained by the partial reduction of the alkali and alkaline-earth tungstates, are usually regarded as compounds of the tungstates with tungsten dioxide, but their exact constitution is as yet unknown. Owing to their bronze-like appearance and insolubility in acids and alkalis, they have been employed as bronze powder substitutes.

They are scarcely affected by aqua regia, but are oxidised by ammoniacal silver nitrate solution, a reaction which is utilised for their analysis. Owing to their insolubility they can be freed from metallic tungsten and its oxides only by successive extractions with aqua regia, hydrochloric acid, potassium carbonate, and water.

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[1] Lotz, *Ann.*, 1854, **91**, 49; Lefort, *Ann. Chim. Phys.*, 1879, [5], **17**, 470; Smith and Dieck, *Zeit. anorg. Chem.*, 1894, **5**, 13; Kantschov, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 729.

[2] Deal, *J. Amer. Chem. Soc.*, 1897, **19**, 213; see also Hallopeau, *Compt. rend.*, 1898, **127**, 57; *Bull. Soc. chim.*, 1899, [3], **21**, 267; Allen and Gottschalk, *Amer. Chem. J.*, 1902, **27**, 328.

[3] Allen and Gottschalk, *Amer. Chem. J.*, 1902, **27**, 328; Benrath, *Zeit. wiss. Photochem.*, 1917, **16**, 253.

Tungsten Sodium Bronze was first obtained by Wöhler by the reduction of sodium tungstate with hydrogen, and may also be obtained by substituting coal-gas, zinc, iron, or tin for hydrogen, or by means of electrolysis. It forms fine golden cubes, which have a specific gravity of 6·617, and conduct electricity well. On ignition in the air, it oxidises and fuses. It is not attacked by any acid except hydrofluoric acid, nor is it acted upon by alkalis except on fusion.[1] According to Philipp,[2] the products are a mixture of different compounds, the relative proportions of which vary according to the method of preparation and the nature of the original tungstate. The substance obtained by heating the ditungstate in hydrogen, which was formerly supposed to have the composition $Na_2W_3O_9$, is, according to Philipp, $Na_5W_6O_{18}$, and has a golden-yellow colour. By the electrolysis of fused sodium paratungstate a blue bronze, $Na_2W_5O_{15}$, is obtained, which forms dark blue cubes or plates having a red reflex. A purple-red bronze, $Na_2W_3O_9$, is obtained by strongly heating a mixture of 12·9 grams of sodium carbonate and 68·9 grams of tungsten trioxide with 20 grams of tinfoil, and a reddish-yellow bronze, $Na_4W_5O_{15}$, by fusing 60–80 grams of a mixture of two molecular proportions of sodium tungstate and one of the trioxide with 30 grams of tinfoil for two hours. It forms reddish-yellow cubes and yields a brownish-yellow powder.

Tungsten Potassium Bronze is obtained in a similar manner to the sodium bronzes, but only one compound[3] appears to exist, $K_2W_4O_{12}$. Bronzes containing lithium and rubidium have also been prepared as well as a number of mixed bronzes containing both sodium and potassium or an alkali metal along with one of the alkaline-earth metal groups.[4]

497 *Phosphotungstic Acids.*—Tungstic acid combines with phosphoric, arsenic, antimonic, and vanadic acids to form complex substances analogous to the corresponding molybdic derivatives. A very large number of these have been prepared, the relation $R_2O_5 : WO_3$ varying from 1 : 7 to 1 : 24. *Phospho-*

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[1] Knorre, *J. pr. Chem.*, 1883, [2], 27, 63.

[2] *Ber.*, 1882, 15, 499.

[3] Schaefer, *Zeit. anorg. Chem.*, 1904, 38, 142, where references to the literature are given; Hallopeau, *Compt. rend.*, 1898, 127, 57; *Bull. Soc. chim.*, 1899, [3], 21, 267.

[4] See Engels, *Zeit. anorg. Chem.*, 1903, 37, 125; Hallopeau, *Compt. rend.*, 1898, 127, 512.

duodecitungstic acid, $H_3PW_{12}O_{40},xH_2O$, is obtained by evaporating a mixture of the requisite quantities of orthophosphoric acid and metatungstic acid, or by the exact decomposition of the barium salt with sulphuric acid or of the mercurous salt with hydrochloric acid. It crystallises in tetragonal pyramids containing water of crystallisation, the amount of which is variously stated by different investigators. Phosphotungstic acid is largely used as a reagent for the precipitation of the alkaloids, proteins, and certain of their hydrolysis products, and also for the detection of potassium and ammonium salts, with which it yields insoluble precipitates. For this purpose it is prepared by acidifying a solution of 4 parts of sodium tungstate and 1 of common sodium phosphate with sulphuric acid and extracting the concentrated solution with ether, in which phosphotungstic acid is readily soluble.[1] Two sodium salts are known, having the formulæ $Na_2HPW_{12}O_{40},xH_2O$ and $Na_3PW_{12}O_{40},xH_2O$, and are obtained by heating together solutions of sodium hydrogen phosphate and tungstate. In presence of an excess of hydrochloric acid the former salt is obtained in yellow crystals, whilst when the acid is gradually added with stirring until crystallisation commences the latter salt separates in transparent colourless octahedra.

The number of complex phosphotungstates and similar compounds is very large, and many of them crystallise well.[2]

498 *Silicotungstic Acids.*—These peculiar compounds were discovered and investigated by Marignac,[3] but the composition of many of them is doubtful.

Silicodecitungstic Acid,

$$H_8W_{10}SiO_{36},3H_2O\ (=4H_2O,SiO_2,10WO_3,3H_2O).$$

—To prepare this acid, gelatinous silica is boiled with ammonium polytungstate and the solution evaporated, ammonia being added from time to time. The *ammonium salt*, $(NH_4)_8SiW_{10}O_{36},8H_2O$, is thus obtained in short, rhombic prisms which are soluble in water; the solution is then precipitated by silver nitrate, and the precipitate washed and decomposed by hydrochloric acid. On evaporating the filtrate in a vacuum the acid is left as a yellowish, glassy mass, and on exposure to air splits into fragments, which then deliquesce. Its salts have not been carefully examined.

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[1] Winterstein, *Chem. Zeit.*, 1898, **22**, 539.

[2] See Scheibler, *Ber.*, 1872, **5**, 801; Sprenger, *J. pr. Chem.*, 1880, [2], **22** 48; Gibbs, *Amer. Chem. J.*, 1880, **2**, 217, 281; 1882, **4**, 377; 1883, **5**, 361, 391; 1885, **7**, 31, 392; Kehrmann, *Ber.*, 1887, **20**, 1805, 1811; 1891, **24** 2326; 1892, **25**, 1966; *Annalen*, 1888, **245**, 45; *Zeit. anorg. Chem.*, 1891, **1** 428; Drechsel, *Ber.*, 1887, **20**, 1452; Péchard, *Compt. rend.*, 1889, **109**, 301 1890, **110**, 754; Hallopeau, *Compt. rend.*, 1896, **123**, 1065; Kehrmann anc Rüttimann, *Zeit. anorg. Chem.*, 1899, **22**, 285; Rogers, *J. Amer. Chem. Soc.* 1903, **25**, 298; Copaux, *Ann. Chim. Phys.*, 1909, [8], **17**, 251; Rosenheim *Zeit. Elektrochem.*, 1911, **17**, 694; Rosenheim and Jaenicke, *Zeit. anorg Chem.*, 1912, **77**, 239; 1917, **101**, 254; Copaux, *Compt. rend.*, 1913, **156**, 71 Prandtl and Hecht, *Zeit. anorg. Chem.*, 1915, **92**, 198; Sweeney, *J. Amer. Chem Soc.*, 1916, **38**, 2377.

[3] *Ann. Chim. Phys.*, 1864, [4], **3**, 5.

On dissolving it in water and evaporating the solution, some silicic acid separates out, and the thick mother-liquor yields short triclinic prisms of *octabasic tungstosilicic acid*, $H_8W_{12}SiO_{42},20H_2O$ ($= 4H_2O,SiO_2,12WO_3,20H_2O$), which are readily soluble in water and alcohol. It forms both normal and acid salts.[1]

Silicoduodecitungstic or *Silicotungstic Acid* was formulated by Marignac as an octabasic acid,

$$H_8SiW_{12}O_{22},29H_2O\ (= 4H_2O,SiO_2,12WO_3,29H_2O),$$

but according to Wyrouboff[2] it is tetrabasic, and has the formula $2H_2O,SiO_2,12WO_3,31H_2O$, the normal salts of Marignac being basic salts and his acid salts in reality the normal salts. All the salts contain water of crystallisation, and in view of the uncertainty as to their constitution are at present best formulated in terms of the oxides. The salts of this acid are formed by boiling gelatinous silicic acid with the polytungstates of the alkali metals. To obtain the acid the salts are precipitated with mercurous nitrate and the washed precipitate is decomposed by hydrochloric acid. It crystallises below 40° in large tetragonal pyramids of the formula $H_8SiW_{12}O_{42},29H_2O$, above 40°, or in presence of hydrochloric acid, in rhombohedral forms, $H_8SiW_{12}O_{42},22H_2O$, and readily dissolves in water, alcohol, or ether. Silicotungstic acid is a valuable reagent for alkaloids.

The salts, with the exception of the mercurous salt and a few others, are soluble in water. Boiling hydrochloric acid converts the normal salts into acid salts without decomposing them further (Marignac), whilst alkalis decompose their solutions with the separation of silicic acid. They have been very thoroughly examined both by Marignac and by Wyrouboff.

Potassium Silicotungstate.—Three distinct salts are known.[3] The salt $4K_2O,SiO_2,12WO_3,14H_2O$ forms hard, granular crusts, consisting of prisms closely resembling cubes; $2K_2O,SiO_2,12WO_3,18H_2O$ forms transparent, glistening, hexagonal crystals; and $3K_2O,2SiO_2,24WO_3,30H_2O$ crystallises in monoclinic prisms.

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[1] See, however, Kehrmann, *Zeit. anorg. Chem.*, 1904, **39**, 98; Rosenheim and Jaenicke, *ibid.*, 1912, **77**, 242; 1917, **101**, 240; Copaux, *Compt. rend.*, 1913, **156**, 71.

[2] *Bull. Soc. franç. Min.*, 1896, **19**, 219.

[3] See also van Liempt, *Zeit. anorg. Chem.*, 1922, **122**, 175.

Marignac formulates the first of these as the normal salt, $K_8SiW_{12}O_{42},14H_2O$, and the others as acid salts, $H_4K_4SiW_{12}O_{42},16H_2O$ and $2H_5K_3SiW_{12}O_{42},25H_2O$, whereas Wyrouboff regards them as a basic salt,

$$K_4SiW_{12}O_{40},4KOH,12H_2O,$$

a normal salt, $K_4SiW_{12}O_{40},18H_2O$, and a double salt,

$$K_4SiW_{12}O_{40},K_2H_2SiW_{12}O_{40},29H_2O.$$

Zircono-,[1] mangano-,[2] boro-,[3] bismutho-,[4] and silico-vanadiotungstates [5] have also been obtained.

Pertungstic Acid.—When a solution of sodium paratungstate is boiled for a few minutes with hydrogen peroxide, a yellowish solution is obtained, which no longer gives a precipitate with nitric acid.[6] When the solution is allowed to evaporate in a vacuum, small white crystals having the formula $NaWO_4,H_2O$ are deposited, which are the sodium salt of the unknown pertungstic acid, HWO_4. The same salt is formed in solution by the electrolysis of slightly acid solutions of sodium tungstate.[7] More highly oxidised compounds are formed by the action of caustic alkali and hydrogen peroxide on a solution of a pertungstate,[8] the unstable salts, Na_2O_2,WO_4,H_2O_2; $Na_2O_2,WO_4,H_2O_2,(Na_2O_2)_2WO_4,7H_2O$; and K_2O_4,WO_4,H_2O having been isolated in this way. Aqueous solutions of pertungstic acid and hydrogen peroxide appear to contain the unstable acids [9] $WO_2(O_2H)_2$ and $WO_2(O_2H)(OH)$.

TUNGSTEN AND THE HALOGENS.

499 *Tungsten Hexafluoride,* WF_6, is formed by the action of anhydrous hydrofluoric acid on tungsten hexachloride in the cold, and can also be prepared by the action of arsenic tri-

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[1] Hallopeau, *Bull. Soc. chim.*, 1896, [3], **15**, 917.

[2] Just, *Ber.*, 1903, **36**, 3619.

[3] Rosenheim and Jaenicke, *Zeit. anorg. Chem.*, 1912, **77**, 239; Rosenheim and Schwer, *ibid.*, 1914, **89**, 224.

[4] Sweeney, *J. Amer. Chem. Soc.*, 1916, **38**, 2377.

[5] Friedheim and Henderson, *Ber.*, 1902, **35**, 3242.

[6] Péchard, *Compt. rend.*, 1891, **112**, 1060.

[7] Thomas, *J. Amer. Chem. Soc.*, 1899, **21**, 373.

[8] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 632.

[9] Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 472.

fluoride or antimony pentafluoride on the hexachloride. The preparation by the last of these methods can be carried out in glass vessels and proceeds according to the equation:

$$WCl_6 + 3SbF_5 = WF_6 + 3SbF_3Cl_2.$$

Antimony pentafluoride is gradually added to the tungsten hexachloride contained in a flask until no further reaction occurs, and the contents of the flask are finally heated to 90°. The hexafluoride volatilises, and is condensed in a receiver cooled by a freezing mixture of alcohol and solid carbon dioxide. A trace of chlorine is present, which can be removed by allowing the liquid in the receiver to boil for a moment.[1]

Pure tungsten hexafluoride is a colourless gas, which has the normal density corresponding with the formula WF_6, and is therefore about ten times as heavy as air. It condenses to a faintly yellow liquid which boils at 19·5° and solidifies at 2·5° to a snow-white mass. It is at once decomposed by water and fumes in the air; nearly all the commoner metals, except gold and platinum, are attacked by it. It is absorbed by alkali fluorides and reacts violently with ammonia.

Tungsten Oxytetrafluoride, WOF_4, can be prepared by the action of anhydrous hydrofluoric acid on the oxytetrachloride in the cold, or by heating tungsten trioxide with lead fluoride to redness in an electric furnace. It sublimes in white plates, melts at 110°, and boils at 185—190°. It is decomposed by water, and is soluble in chloroform, absolute alcohol, or benzene. It appears to unite with ammonia, forming an orange-coloured substance (Ruff).

Tungsten Dioxydifluoride, WO_2F_2, has not been prepared pure, but is formed in small amount by the action of moisture on the vapour of the oxytetrafluoride. Double salts with the alkali fluorides, such as $2KF,WO_2F_2,H_2O$, have, however, been prepared by the action of hydrofluoric acid on the tungstates.[2] A double salt of the formula KF,WO_2F_2,H_2O is also known.

500 Four compounds of tungsten and chlorine are known, viz.:

Tungsten dichloride	WCl_2.
Tungsten tetrachloride . . .	WCl_4.
Tungsten pentachloride . .	WCl_5.
Tungsten hexachloride . . .	WCl_6.

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[1] Ruff and Eisner, *Ber.*, 1905, **38**, 742; Ruff, Eisner, and Heller, *Zeit. anorg. Chem.*, 1907, **52**, 256.

[2] Marignac, *Ann. Chim. Phys.*, 1863, [3], **69**, 70.

Tungsten Dichloride, WCl_2.—This body may be obtained in pale grey crusts by reducing the hexachloride in hydrogen at a moderately high temperature, or by reduction in a stream of nitrogen with powdered aluminium and quartz.[1] It is, however, best prepared by heating the tetrachloride in a current of carbon dioxide at the temperature of a moderately hot zinc bath. The dichloride is a non-volatile, loose, grey powder without lustre or crystalline structure. It alters perceptibly on short exposure to the air and dissolves slightly in water, forming a brown solution. The remainder is converted into the brown oxide, a slow evolution of hydrogen occurring (Roscoe). In view of the fact that a compound of the formula $W_3Cl_6,HCl,4{\cdot}5H_2O$ has been prepared,[2] the dichloride may perhaps be regarded as having the composition W_3Cl_6.

Tungsten Trichloride.—Although this compound has not been obtained, double salts of the form $M_3W_2Cl_9$ have been prepared by reduction of tungstic acid in hydrochloric acid solution in presence of alkali chloride.[3]

Tungsten Tetrachloride, WCl_4, is produced by the incomplete reduction of the hexachloride or pentachloride by hydrogen, and forms the non-volatile residue obtained by the distillation of the hexachloride in hydrogen. In order to obtain it in the pure state a mixture of hexa- and penta-chloride is distilled at a low temperature from a bath of sulphuric acid in a current of dry hydrogen or carbon dioxide, and the volatile pentachloride poured back again once or twice over the residue to convert into the tetrachloride the lower chlorides or metal which are also formed. Tungsten tetrachloride is a loose, soft, crystalline powder of a greyish-brown colour. It is highly hygroscopic, though not so much so as the pentachloride, and is partially decomposed by cold water into the brown oxide and hydrochloric acid. The tetrachloride is non-volatile and infusible under ordinary pressure, but on heating it decomposes into pentachloride, which distils off, and dichloride, which remains behind. On heating in hydrogen to a temperature above the melting point of zinc the tetrachloride is reduced to metallic tungsten, some of which is deposited as a black, tinder-like powder and undergoes spontaneous ignition on exposure to air (Roscoe). By reduction of an acidified solution of tungstic acid in presence of alkali chloride, Olsson[4] has prepared the compound $K_2W(OH)Cl_5$.

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[1] Lindner and others, *Ber.*, 1922, **55**, [*B*], 1458.

[2] Hill, *J. Amer. Chem. Soc.*, 1917, **39**, 2383.

[3] Olsson, *Ber.*, 1913, **46**, 566; Rosenheim and Dehn, *ibid.*, 1915, **48**, 1167.

[4] *Loc. cit.*

Tungsten Pentachloride, WCl_5.—This compound is formed by the incomplete reduction of the hexachloride in a current of hydrogen. If the temperature be kept but slightly above the boiling point of the hexachloride, the dark red colour of its vapour is seen to disappear and a light greenish-coloured vapour takes its place, and this soon condenses either to black drops or to long, lustrous, black, needle-shaped crystals. After two or three distillations in hydrogen a pure volatile product is obtained. For the production of the pentachloride, it is, however, more convenient to reduce the hexachloride at a higher temperature, when a further loss of chlorine takes place, the solid non-volatile tetrachloride remaining behind and the volatile pentachloride distilling over. The latter compound only requires redistillation in order to be obtained in the pure state. Tungsten pentachloride crystallises in long, black, lustrous crystals, but if quickly condensed the crystalline powder possesses a dark green colour, resembling potassium manganate. It melts at 248°, boils at 275·6°, has the normal vapour density at 350°, and is extremely hygroscopic, the crystals becoming instantly covered with a dark golden-green film on exposure to air, whilst the small particles are converted into liquid. The crystals do not decrepitate on cooling like those of the hexachloride. On treatment with large quantities of water, the pentachloride forms an olive-green solution, although the greater part is at once decomposed into the blue oxide and hydrochloric acid.

Electrolysis of a solution of the hexachloride[1] in absolute alcohol gives a compound of quinquevalent tungsten of the formula $[WCl_2(OC_2H_5)_3]_2$.

Although the oxychloride, $WOCl_3$, is unknown, two series of *chlorotungstites* have been prepared, having respectively the formulæ[2] M_2WOCl_5 and $MWOCl_4$.

Tungsten Hexachloride, WCl_6.—This substance is prepared by heating metallic tungsten in an excess of dry and pure chlorine; platinum black may be employed as a catalyst.[3] It is necessary for the preparation of the pure compound that every trace of oxygen and of moisture be excluded, as otherwise some red oxychloride is invariably formed, and this cannot easily be separated from the hexachloride by distillation. Metallic tungsten takes fire at a moderate heat in dry chlorine, and the action goes on by itself until all the chlorine has disappeared.

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[1] Fischer and Roderburg, *Zeit. anorg. Chem.*, 1913, **81**, 170; Fischer and Michiels, *ibid.*, 1913, **81**, 102.

[2] Collenberg, *Zeit. anorg. Chem.*, 1918, **102**, 247; *Arkiv Kem. Min. Geol.*, 1918, **7**, No. 5, 1.

[3] Hill, *J. Amer. Chem. Soc.*, 1916, **38**, 2383.

In order to obtain the hexachloride in quantity, the metal is first ignited in a current of dry hydrogen; then the hydrogen is completely displaced by a current of dry carbon dioxide, and lastly chlorine free from air substituted, and the tube or retort moderately heated. At the commencement of the operation a slight sublimate of red, needle-shaped crystals of the oxychloride is frequently formed owing to the unavoidable presence of traces of oxygen, but this is easily driven to the end of the tube beyond the point at which it is intended to collect the hexachloride. On raising the temperature of the metal, a granular sublimate of dark violet, opaque crystals of the hexachloride makes its appearance, and if in large quantity the hexachloride collects as a blackish-red liquid. In order to saturate this liquid, it is slowly distilled in a current of chlorine. The dark violet crystals decrepitate on cooling, and the crystalline mass thus readily breaks up into a powder.

Perhaps the simplest method of preparing the hexachloride consists in the interaction of tungsten trioxide and carbon tetrachloride at 280°.[1]

When pure, the solid hexachloride does not undergo any change even in moist air, but in the presence of the slightest trace of oxychloride it at once absorbs moisture, evolving copious fumes of hydrogen chloride and changing in colour from violet to brown. Water does not act upon the pure hexachloride, but on boiling decomposition occurs. If, however, the oxychloride be present the whole is suddenly decomposed by cold water into a greenish oxide. It is soluble in carbon disulphide and crystallises from the solution in six-sided plates.

The melting point of the hexachloride is 275°; it boils under a pressure of 759·5 mm. at 346·7°. The vapour density of tungsten hexachloride has been determined in sulphur vapour and in mercury vapour; at 440°, the mean experimental density compared with that of hydrogen is 168·8, whilst at 350° the density is 190·9, the calculated density being 196·9. The alteration of the density from 191 at 350°, only 3° above the boiling point, to 169 at 440° points to the fact that dissociation occurs. That this is the case is shown by the fact that when a current of dry carbon dioxide is passed through the fused hexachloride a continuous liberation of chlorine takes place, whereas the pentachloride treated in the same way does not undergo a similar decomposition.

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[1] Michael and Murphy, *Amer. Chem. J.*, 1910, **44**, 365.

Tungsten Oxychlorides.—The *oxytetrachloride*, $WOCl_4$, and the *dioxydichloride*, WO_2Cl_2, have been studied by Blomstrand and Riche. The dioxydichloride is best obtained by passing chlorine over the brown oxide, WO_2. Combination takes place at a moderate temperature, the oxide becoming covered with a whitish crust, which as the temperature increases sublimes without melting, condensing in small square scales of a light lemon-yellow colour. The dioxydichloride volatilises at a temperature approaching redness with partial decomposition; the crystals do not fuse, and are not acted upon by moist air or cold water. Even when boiled with water the dioxydichloride is not completely decomposed.

The splendid red needle-shaped crystals of the oxytetrachloride, prepared by Wöhler, are obtained by passing the hexachloride vapour over heated oxide or dioxydichloride:

$$WO_3 + 2WCl_6 = 3WOCl_4,$$

and also by acting on the trioxide with phosphorus pentachloride,[1] and by the interaction of tungsten trioxide with a solution of chlorine in carbon tetrachloride at 240°.[2] Attempts to prepare tungsten dichloride by interaction of the metal with carbonyl chloride result in the formation of this compound.[3] The crystals melt at 210·4°, and the liquid boils at 227·5°, forming a red vapour rather lighter coloured than that of the hexachloride, and having the normal density at 350° (Roscoe). On repeated distillation over red hot charcoal in a current of chlorine the hexachloride is formed. On exposure to the air the oxytetrachloride becomes at once covered with a yellowish crust of tungstic acid.

501 Bromine acts rapidly on red-hot tungsten, forming dark, bromine-like vapours, which condense to a crystalline sublimate. Special precautions similar to those taken in the preparation of the chlorides must also be employed for the bromides, as the oxybromides formed in the presence of air and moisture possess almost the same colour as the bromide, and therefore the detection of the impurity is not so easy as with the chloride.

Tungsten Dibromide, WBr_2, is formed by the reduction in hydrogen of the pentabromide, heated in a bath of fused zinc chloride. A residue of non-volatile dibromide remains in the form of a bluish-black, velvety, crystalline powder.

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[1] Schiff, *Ann.*, 1879, 197, 185.

[2] Michael and Murphy, *loc. cit.*

[3] Lindner and others, *Ber.*, 1922, 55, [*B*], 1458.

Tungsten Pentabromide, WBr_5, is prepared by the action of an excess of bromine on tungsten, and is formed also when the hexachloride is heated in dry hydrogen bromide, but cannot be prepared pure in this way.[1] The pentabromide forms dark crystals having a metallic lustre resembling iodine, melting at 276°, and boiling at 333°. It is at once decomposed by an excess of water into hydrobromic acid and the blue oxide. When the pentabromide is heated in a current of hydrogen, the metal is formed in the state of pyrophoric powder.

Tungsten Hexabromide, WBr_6, is obtained, according to Schaffer and Smith,[2] by gently heating tungsten in dry bromine vapour in an atmosphere of nitrogen. It can be sublimed, and forms bluish-black needles. It decomposes very readily when heated, fumes in the air, and is decomposed by water with formation of a blue oxide.

Liquefied hydrogen bromide converts the hexachloride at 60—70° into a mass of olive-green crystals which melt at 232° and have the composition $WCl_6,3WBr_6$, whilst at the ordinary temperature a similar substance of the composition WCl_6,WBr_6 is formed (Defacqz).

Tungsten oxybromides, corresponding to the oxychlorides, exist. The *dioxydibromide*, WO_2Br_2, is prepared by passing bromine vapour over red hot tungsten dioxide. It forms light red, transparent crystals which yield a yellow powder. It does not melt, but volatilises at a temperature approaching a red heat, and is not acted upon by water. The *oxytetrabromide*, $WOBr_4$, is formed in the same circumstances as the last-named compound in brownish-black, lustrous needles, which are readily fusible and can be separated from the dioxydibromide by gently heating, when the latter compound remains behind. It melts at 277°, boils at 327·5°, and is decomposed by water.

Tungsten Di-iodide, WI_2, is obtained in the form of green, metallic scales when iodine vapour is passed over the metal heated to redness [3] (Roscoe), and is formed also by the action of hydrogen idoide on the hexachloride at 400° (Defacqz).[4]

Tungsten Tetra-iodide, WI_4, obtained by Defacqz[5] by the action of liquefied hydrogen iodide on the hexachloride at 100°, is a black, infusible, crystalline mass, which is decomposed by water into the brown oxide and hydriodic acid.

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[1] Defacqz, *Ann. Chim. Phys.*, 1901, [7], **22**, 247.

[2] *J. Amer. Chem. Soc.*, 1897, **18**, 1098.

[3] *Ann.*, 1872, **162**, 349.

[4] *Ann. Chim. Phys.*, 1901, [7], **22**, 239.

[5] *Loc. cit.*

TUNGSTEN AND SULPHUR.

502 *Tungsten Disulphide*, WS_2, is obtained by the action of sulphur, hydrogen sulphide, or carbon disulphide on ignited metallic tungsten. It may be prepared also by heating tungsten trioxide in a crucible with six times its weight of cinnabar or with potassium carbonate and sulphur, and by heating the hexachloride in a current of hydrogen sulphide (Defacqz). It forms soft, black, needle-shaped crystals which soil the fingers like graphite.

A *chlorosulphide*, $WCl_6,3WS_3$, is formed, by the action of liquefied hydrogen sulphide on the hexachloride at 60° (Defacqz).

Tungsten Trisulphide, WS_3, is obtained only in the wet way by dissolving tungsten trioxide in ammonium sulphide and precipitating with an acid, or by saturating an aqueous solution of an alkali tungstate with hydrogen sulphide, and acidifying. When dry it is black, yielding a liver-coloured powder. It yields a colloidal solution with water, and is precipitated by ammonium chloride and acids. It is easily dissolved by potassium carbonate and also by ammonia. Heated with potassium cyanide, it forms the disulphide; this is unaltered by fusion with excess of the reagent.

The Thiotungstates.—The thiotungstates of the alkali and alkaline-earth metals are prepared by dissolving the trisulphide in the corresponding hydrosulphide, or by treating the corresponding tungstate with hydrogen sulphide. The ammonium salt, $(NH_4)_2WS_4$, is deposited from concentrated solution in yellowish-red crystals; the potassium salt, K_2WS_4, forms anhydrous, yellow crystals, whilst the sodium salt, Na_2WS_4, crystallises with difficulty. Salts of the form $M_2WO_2S_2$ and a salt of the composition K_2WO_3S,H_2O are also known.

TUNGSTEN AND NITROGEN, PHOSPHORUS, CARBON, SILICON, AND BORON.

503 Tungsten does not combine directly under ordinary conditions with nitrogen, and neither the metal nor the dioxide is attacked when strongly heated in ammonia.[1] By the action

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[1] Langmuir, *J. Amer. Chem. Soc.*, 1913, **35**, 931; 1915, **37**, 1139, has, however, shown that under the conditions obtaining in a nitrogen-filled tungsten-filament electric incandescence lamp, a nitride, WN_2, is formed.

of ammonia on the oxytetrachloride or the hexachloride in the cold, a black, semi-metallic powder is obtained, which has the composition W_2N_3. It is insoluble in caustic soda, nitric acid, or dilute sulphuric acid, but is converted by concentrated sulphuric acid into ammonia and tungstic acid.[1]

By the action of ammonia on tungsten trioxide at a dull red heat Wöhler obtained a black, amorphous product which he termed "*tungsten nitretamidoxide,*" the formula of which is $W_5N_6H_3O_5$ (Rideal). It is insoluble in acids and alkalis, but dissolves in sodium hypochlorite solution, and on ignition decomposes, ammonia, nitrogen, and hydrogen being evolved. Other compounds which have been described are: $W_4N_4H_2O_4$, $W_3N_6H_4$, $W_3N_4H_4$, and W_3N_2.

Phosphides of Tungsten.—Phosphorus and tungsten combine directly when the finely powdered metal is heated to redness in phosphorus vapour, a dark green powder of the composition W_3P_4 being formed. Another compound, W_2P, is obtained, when a mixture of phosphorus pentoxide and tungsten trioxide, in the proportion of two molecules of the former to one molecule of the latter, is reduced at a high temperature in a charcoal crucible,[2] and forms a vesicular mass, the hollow portions of which contain large crystals.

A black, amorphous *diphosphide*, WP_2, is formed when the hexachloride is heated in phosphine, and this reacts with copper phosphide at a high temperature to form *tungsten monophosphide*, WP, which crystallises in grey prisms with a metallic reflex, has density 8·5, and is oxidised to tungsten trioxide when heated in air (Defacqz). An *arsenide*, WAs_2, has also been prepared in a similar manner to the diphosphide, which it resembles.

Tungsten and Carbon.—Tungsten forms two carbides. The compound obtained by heating the oxide with carbon or calcium carbide[3] has the formula W_2C, whilst in presence of a large amount of iron[4] the carbide WC is produced. They are both hard, iron-grey, crystalline substances. The compound W_3C is also considered to be definite.[5] Several complex carbides containing iron or chromium have also been prepared,[1] and the existence of a compound WCO is postulated.[2]

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[1] Wöhler, *Ann.*, 1850, **73**, 190; 1858, **105**, 258; Rideal, *Journ. Chem. Soc.*, 1889, **55**, 41.

[2] Wöhler, *Journ. Chem. Soc.*, 1853, **8**, 94.

[3] Moissan, *Compt. rend.*, 1896, **123**, 13; 1897, **125**, 839.

[4] Williams, *Compt. rend.*, 1898, **126**, 1722.

[5] Ruff and Wunsch, *Zeit. anorg. Chem.*, 1914, **85**, 292. See also Hilpert and Ornstein, *Ber.*, 1913, **46**, 1669.

Quadrivalent tungsten forms a series of double cyanides of the general formula $R_4[W(CN)_8],xH_2O$; quinquevalent tungsten forms a series of double cyanides of the type $R_3[W(CN)_8],xH_2O$, double thiocyanates, and double oxalates; in none of these cases, however, is the constituent simple tungsten salt known.

Tungsten Silicide, W_2Si_3, is obtained by heating the trioxide with silicon in the electric furnace,[3] and freeing the product from metal by electrolytic oxidation. It forms beautiful, steel-grey plates with a metallic lustre, and burns in oxygen. It is attacked by a mixture of nitric and hydrofluoric acids, and by fused potash. Other silicides which have been described are WSi_2 and WSi_3.

Tungsten Boride, WB_2, is obtained by fusing the two elements together by a convenient electrical method; it crystallises in hard octahedra of density 10·77.[4] It is attacked by concentrated acids.[5]

DETECTION AND ESTIMATION OF TUNGSTEN.[6]

504 All the insoluble tungsten compounds can be converted into soluble tungstates by fusion, either with caustic alkali alone, or with the addition of nitre. The solution when brought into contact with zinc or aluminium[7] and hydrochloric acid becomes blue-coloured, owing to the formation of the blue tungsten oxides (or tungsten tungstates). When ammonium sulphide is added to the colourless solution of the tungstate, and then dilute hydrochloric acid, a brown precipitate of tungsten sulphide is obtained, whereas hydrochloric acid alone precipitates tungstic acid, which on heating turns yellow. If the tungsten compounds are fused with a small quantity of tin in the reducing flame with microcosmic salt, a blue bead is obtained, whilst

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[1] *Compt. rend.*, 1898, **127**, 1410; 1899, **128**, 207; 1903, **137**, 292.

[2] Langmuir, *J. Amer. Chem. Soc.*, 1915, **37**, 1139.

[3] Vigouroux, *Compt. rend.*, 1898, **127**, 393. See also Warren, *Chem. News*, 1898, **78**, 318.

[4] Wedekind, *Ber.*, 1913, **46**, 1198.

[5] Tucker and Moody, *Journ. Chem. Soc.*, 1902, **81**, 16.

[6] The arc spectrum of tungsten has been examined by Belke, *Zeit. wiss. Photochem.*, 1917, **17**, 132, 145, and the *X*-ray spectrum by Barnes, *Phil. Mag.*, 1915, [6], **30**, 368; Ledoux-Lebard and Dauvillier, *Compt. rend.*, 1917, **164**, 687; Siegbahn, *Phil. Mag.*, 1919, [6], **38**, 639; de Broglie, *Compt. rend.*, 1919, **169**, 962; Duane and Patterson, *Phys. Rev.*, 1920, **16**, 526.

[7] Torossian, *Amer. J. Sci.*, 1914, [4], **38**, 537.

tungsten compounds containing iron yield in the reducing flame a blood-red bead. Tungstic oxide can be very readily detected by fusing with potassium bisulphate and adding sulphuric acid and a crystal of phenol or quinol (hydroquinone), when a blue or violet coloration is produced, by the aid of which the presence of 0·002 mgm. of tungstic oxide can be recognised (Defacqz).

Tungsten is estimated *gravimetrically* as the trioxide. For the purpose of ascertaining the quantity contained in wolfram, for instance, the finely powdered mineral is heated with aqua regia, evaporated to dryness, the residue treated with water, the soluble chlorides of iron and manganese are filtered off, and the insoluble tungstic acid is washed with alcohol and dissolved in ammonia. The solution is then evaporated down, and the residue heated gently, and afterwards ignited in presence of air, when the trioxide remains, and is weighed. Solutions of tungstates may also be precipitated with benzidine hydrochloride,[1] mercurous nitrate,[2] or "nitron,"[3] and the precipitate ignited and weighed as the trioxide (compare also Wolter).[4] Colorimetric methods, in which titanous chloride[5] or stannous chloride[6] are employed, may also be used.

For recent investigations on the estimation of tungsten the original literature should be consulted.[7]

Atomic Weight of Tungsten.—The atomic weight of tungsten has been determined by numerous investigators. Schneider,[8] by the reduction of tungsten trioxide to metal and oxidation of the metal to trioxide, found the average value 184·11, whilst

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[1] v. Knorre, *Ber.*, 1905, **38**, 783; Kantschev, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 729.

[2] Defacqz, *Compt. rend.*, 1896, **123**, 308.

[3] Gutbier and Weise, *Zeit. anal. Chem.*, 1914, **53**, 426.

[4] *Chem. Zeit.*, 1910, **35**, 2.

[5] Travers, *Compt. rend.*, 1918, **166**, 416.

[6] Heath, *Chem. Trade J.*, 1920, **66**, 629.

[7] Hilpert and Dieckmann, *Ber.*, 1913, **46**, 152; Treadwell, *Zeit. Elektrochem.*, 1913, **19**, 219, 381; Zinberg, *Zeit. anal. Chem.*, 1913, **52**, 529; Hermann, *ibid.*, 1913, **52**, 557; Kafka, *ibid.*, 1912, **52**, 601; Wunder and Schapira, *Ann. Chim. anal.*, 1913, **18**, 257; Arnold, *Zeit. anorg. Chem.*, 1914, **88**, 74, 333; Dieckmann and Hilpert, *Ber.*, 1914, **47**, 2444; Marbaker, *J. Amer. Chem. Soc.*, 1915, **37**, 86; Dittler and Graffenried, *Chem. Zeit.*, 1916, **40**, 681; Guglialmelli and Hordh, *Anal. Soc. Quim. Argentina*, 1917, **5**, 81; Travers, *Compt. rend.*, 1917, **165**, 408; Sweeney, *J. Amer. Chem. Soc.*, 1916, **38**, 2377; van Duin, *Chem. Weekblad*, 1917, **14**, 169; Fenner, *Chem. Zeit.*, 1918, **42**, 403; Jannasch and Leiste, *J. pr. Chem.*, 1918, [2], **97**, 141; Hodes, *Zeit. angew. Chem.*, 1917, **30**, 240; Erlich, *Ann. Chim. anal.*, 1920, [2], **2**, 102; Corti, *Anal. Soc. Quim. Argentina*, 1917, **5**, 308; Löwy, *Zeit. angew. Chem.*, 1919, **32**, 379.

[8] *J. pr. Chem.*, 1850, **50**, 152.

Marchand[1] found an almost identical value. Roscoe[2] by the same method obtained the number 183·48, and by the analysis of the hexachloride the number 184·02, whilst Waddell[3] by the reduction of the trioxide found the higher number 184·33. More recently Pennington and Smith and Desi[4] have found the still higher number 184·8 by Schneider's method, but their results have been criticised by Schneider[5] as untrustworthy. The investigations carried out by Smith and Exner,[6] who converted the hexachloride into the trioxide by the action of water and synthesised the trioxide from the metal, gave an average value for the atomic weight of 184·06. The best mean value is probably 184·1 ± 0·1. The value now (1922) adopted is 184·0.[7]

URANIUM. U = 238·2. At. No. 92.

505 The mineral known as pitchblende was formerly believed by certain chemists to be an ore of either zinc or iron, whilst by others it was thought to contain tungsten. Klaproth, in 1789, was the first to point out the existence in this mineral of a peculiar metal, to which he gave the name of uranium, in remembrance of Herschel's discovery of the planet Uranus in the year 1781. The substance obtained by Klaproth by the reduction of the calx of uranium was supposed by all the chemists who subsequently investigated the subject to be the metal, until Péligot[8] in 1842 proved it to be an oxide. Péligot likewise isolated the metal and determined its equivalent.

Uranium is not a very abundant element, and its chief ore is pitchblende or uraninite. This consists of impure uranoso-uranic oxide, U_3O_8, and is found in Cornwall, at Joachimsthal, Johanngeorgenstadt, Adrianople, and other localities. Carnotite, potassium uranyl vanadate, is found in Colorado, Utah, and S. Australia; autunite, uranyl calcium phosphate, is found in France, Portugal, the United States, and Madagascar. Varieties found in Cornwall are called bassetite and uranospathite.[9]

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[1] *Ann.*, 1851, **77**, 261.

[2] *Mem. Manch. Phil. Soc.*, [3], **5**, 77; *Annalen*, 1872, **162**, 366.

[3] *Amer. Chem. J.*, 1886, **8**, 280.

[4] *Zeit. anorg. Chem.*, 1895, **8**, 198, 205.

[5] *J. pr. Chem.*, 1896, [2], **53**, 288.

[6] *J. Amer. Chem. Soc.*, 1904, **26**, 1082.

[7] Gerber, *Mon. Sci.*, 1917, [5], **7**, 73, claims that tungsten is not a simple substance, but is accompanied by *neotungsten* of higher atomic weight.

[8] *Ann. Chim. Phys.*, 1842, [3], **5**, 5.

[9] Hallimond, *Min. Mag.*, 1915, **17**, 221.

Uranium is found also as a double phosphate with copper in torbernite or uranium-mica, as carbonate in liebigite, voglite, and uranothallite, whilst as uranotantalite or samarskite it is found combined with columbium and tantalum. Other uranium minerals are gilpinite,[1] brannerite,[2] becquerelite,[3] $UO_3,2H_2O$, and soddite,[3] $12UO_3,5SiO_2,14H_2O$. Pitchblende is the best source of uranium, this mineral usually containing from 40 to 90 per cent. of uranoso-uranic oxide, U_3O_8. The following analysis[4] gives the composition of a specimen of pitchblende from Connecticut: UO_3, 26·48 per cent.; UO_2, 57·43; ThO_2, 9·79; CeO_2, 0·25; $(La,Di)_2O_3$, 0·13; $(Y,Er)_2O_3$, 0·20; Fe_2O_3, 0·40; PbO, 3·26; MnO, trace; CaO, 0·08; alkalies, trace; H_2O, 0·61; SiO_2, 0·16; insoluble, 0·70. Total 99·49 per cent.

The uranium minerals always contain the radioactive element radium, as well as helium, the occurrence of which is discussed under the heading of Radioactive Elements. Small amounts of compounds of copper, bismuth, silver, zinc, arsenic, and aluminium are often present.

The process employed for the extraction of uranium from pitchblende is described by Meyer[5] as follows: The finely ground mineral is first roasted and then calcined with sodium carbonate in a reverberatory furnace, the soluble uranium compound being extracted from the melt with water; alternatively, the mineral may be decomposed by fusion with sodium sulphate, followed by extraction of the melt with dilute sulphuric acid, or the mineral may be decomposed with a mixture of sulphuric and nitric acids. In all cases the uranium compounds pass into solution, and in presence of excess of sodium carbonate remain in solution as sodium uranyl carbonate; on boiling with a suitable excess of dilute sulphuric acid, a yellow precipitate of sodium uranate, $Na_2U_2O_7,6H_2O$, is obtained. The insoluble residue contains the radium salt in admixture with a number of other compounds.

The method recommended by Wöhler[6] consists of the decomposition of the pitchblende with a mixture of sulphuri and nitric acids, volatilisation of the acid, and extractio with water, yielding a solution through which hydroge sulphide is passed; the filtrate, after being oxidised with nitric acid, is treated with ammonia, and the precipitate digested with a concentrated solution of ammonium carbonate containing excess of ammonia. Uranic hydroxide dissolves and yellow ammonium uranyl carbonate crystallises out on cooling. Péligot's[1] method depends on the facility with which uranyl nitrate crystallises, and on its ready solubility in ether.

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[1] Larsen and Brown, *Amer. Min.*, 1917, **2**, 75.

[2] Hess and Wells, *J. Franklin Inst.*, 1920, **189**, 225.

[3] Schoep, *Compt. rend.*, 1922, **174**, 1066, 1240.

[4] Clarke, "*The Data of Geochemistry*," *U.S. Geol. Survey Bull.*, 1916, No. 616

[5] Abegg's "*Handbuch der anorganischen Chemie*," 1921, IV, [1], ii, p. 89

[6] *Pogg. Ann.*, 1845, **64**, 94.

Metallic uranium was first prepared in the pure state by Péligot, who obtained it by the action of sodium or potassium on uranium tetrachloride, a mixture of the tetrachloride, potassium chloride, and sodium being usually employed.[2] It is also obtained by heating 500 parts of the oxide, U_3O_8, with 40 parts of sugar charcoal in the electric furnace in a carbon tube, closed at one end. The product contains a little carbon, which is partially removed by heating it in a crucible brasqued with uranium oxide, and enclosed in a larger crucible brasqued with titanium to protect the uranium from the action of nitrogen.[3] Uranium may also be obtained by heating the dioxide to redness with carbon and starting the reduction by means of a cartridge of magnesium and barium dioxide,[4] or by reducing the trioxide with aluminium, a fused regulus of the metal containing a little aluminium being thus obtained.[5] A satisfactory method consists in first preparing the tetrachloride by passing chlorine over the heated dioxide mixed with carbon, or by heating the oxide in a stream of chlorine and sulphur chloride, and then reducing this with sodium or magnesium.[6]

Pure uranium has a white colour, and takes a high polish; it has a density of 18·7 at 14°, and a specific heat of 0·02765; in the powdered state it oxidises on exposure to the air and, if freshly prepared, may be spontaneously inflammable. It decomposes water slowly at the ordinary temperature, and more quickly at the boiling point. In the same condition it burns in oxygen at 170°, in fluorine at the ordinary temperature, in chlorine at 180°, in bromine at 210°, in iodine at about 260°, and in sulphur vapour at 500°. It melts at a high temperature, and has a higher boiling point than iron, condensing in small, non-magnetic spheres, free from carbon.[1] It readily combines with nitrogen at 1000°. Uranium has a potential between those of copper and hydrogen.[2]

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[1] *Ann. Chim. Phys.*, 1842, [3], **5**, 5; 1844, **12**, 549; 1846, **22**, 329; 1869, [4], **17**, 368.

[2] *Ibid.*, 1869, [4], **17**, 368.

[3] Moissan, *Compt. rend.*, 1896, **122**, 1088.

[4] Aloy, *Bull. Soc. chim.*, 1901, [3], **25**, 344.

[5] Stavenhagen, *Ber.*, 1899, **32**, 3065; Stavenhagen and Schuchard, *ibid.*, 1902, **35**, 909.

[6] Rideal, *J. Soc. Chem. Ind.*, 1914, **33**, 673; Lely and Hamburger, *Zeit. anorg. Chem.*, 1914, **87**, 209; Baragiola, *Schweiz. apoth. Zeit.*, 1915, **53**, 477.

Several alloys with iron, manganese, and cobalt have been prepared by the aluminium reduction method. An amalgam[3] can be obtained by the electrolytic method, and leaves pyrophoric uranium when the mercury is distilled off at 242°.

Metallic uranium and its compounds are radioactive (see the section on the Radioactive Elements).

COMPOUNDS OF URANIUM.

URANIUM AND OXYGEN.

506 Uranium combines with oxygen to form two[4] well-defined oxides, UO_2 and UO_3, and these combine, forming intermediate oxides. Both these oxides are more magnetic than the metal.[5] The dioxide is a basic oxide, and gives rise to the uranous salts, in which the metal is quadrivalent. The trioxide, like the corresponding oxide of the other metals of this group, behaves as an acid-forming oxide, yielding salts known as the *uranates*, analogous to the chromates, molybdates, and tungstates. Like the other trioxides of the group, uranium trioxide also yields a large number of derivatives in which only one of the three oxygen atoms is replaced by negative groups; these may be regarded as derivatives of the bivalent compound radicle *uranyl*, UO_2. This radicle has more decidedly basic properties than the corresponding radicles derived from the other metals, and the derivatives, therefore, correspond to the salts of a basic oxide, whilst the similar compounds of the other metals are more nearly allied to the acid chlorides, such as sulphuryl chloride, SO_2Cl_2, and phosphoryl chloride, $POCl_3$. This view of the constitution of the uranyl salts is supported by the electrochemical properties of their solutions. In aqueous solution the salts of strong acids, $UO_2{\cdot}R^I_2$, are hydrolysed to a small extent, corresponding in this respect to the analogous salts of aluminium

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[1] Zimmermann, *Annalen*, 1883, **216**, 1; Moissan, *Compt. rend.*, 1893, **116**, 1429; 1896, **122**, 1088; 1906, **142**, 425.

[2] Fischer and Roderburg, *Zeit. anorg. Chem.*, 1913, **81**, 170; Fischer and Rideal, *ibid.*

[3] Férée, *Bull. Soc. chim.* 1901, [3], **25**, 622.

[4] See Lebeau, *Compt. rend.*, 1922, **174**, 388.

[5] Wedekind and Horst, *Ber.*, 1915, **48**, 105.

and glucinum. The non-hydrolysed portion of the salt dissociates in the normal manner, and on electrolysis the uranyl ion migrates to the cathode. Complex derivatives are, however, very readily formed, especially with salts of organic acids.[1]

Uranium Dioxide, UO_2.—This oxide, formerly mistaken for the metal uranium, is prepared on the technical scale by fusing 35 parts of sodium chloride, 20 parts of sodium uranate, and 1 part of powdered charcoal in a cast steel pot at a red heat, lixiviating with water and treating the residue with hydrochloric acid.[2] It is obtained by heating uranoso-uranic oxide, U_3O_8, or uranic oxalate in a current of hydrogen, or by the electrolysis of uranyl nitrate solution under suitable conditions.[3] Thus prepared it is a pyrophoric powder, having a brown or copper-red colour, and a density of 10·95. When heated in the air it takes fire, and is completely converted into the oxide, U_3O_8.[4] It dissolves in strong acids, forming the green uranous salts.[5] It may be obtained in jet black octahedra isomorphous with thoria by fusing with borax, and then removing the latter with dilute hydrochloric acid.[6] It is also formed in microscopic, black, non-pyrophoric crystals when crystalline uranic hydroxide is reduced in hydrogen,[7] and is left as a brick-red mass, which becomes black on heating, when uranyl bromide is heated in the air.[8]

Uranous oxide is oxidised to the trioxide by ammoniacal silver solutions.[9]

Uranous Hydroxide, $UO_2,2H_2O$ (?), is precipitated in reddish-brown flakes, which become black on ebullition, by adding an alkali to a uranous solution.[10] In presence of alcohol, uranyl salts are reduced by light to uranous salts, or uranous hydroxide. It dissolves easily in dilute acids, whilst the calcined oxide is only slightly soluble in these liquids. The substance has also been obtained electrolytically in a colloidal form.[1]

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[1] Dittrich, *Zeit. physikal. Chem.*, 1899, **29**, 449; Ley, *ibid.*, 1900, **30**, 193; *Ber.*, 1900, **33**, 2658. Compare Kohlschütter, *Annalen*, 1900, **311**, 1.

[2] Parsons, *J. Ind. Eng. Chem.*, 1917, **9**, 466.

[3] Oechsner de Coninck and Camo, *Bull. Acad. roy. Belg.*, 1901, 321.

[4] Jolibois and Bossuet, *Compt. rend.*, 1922, **174**, 386. Oechsner de Coninck, *Bull Soc. chim.*, 1912, [4], **11**, 1037 states that the oxide U_4O_{10} is thus formed.

[5] See Colani, *Compt. rend.*, 1912, **155**, 1249; Raynaud, *ibid.*, 1911, **153**, 1480; *Bull. Soc. chim.*, 1912, [4], **11**, 802.

[6] Hillebrand, *Zeit. anorg. Chem.*, 1893, **3**, 240.

[7] Aloy, *Bull. Soc. chim.*, 1900, [3], **23**, 368.

[8] Oechsner de Coninck, *Compt. rend.*, 1902, **135**, 900.

[9] Smith and Shinn, *Zeit. anorg. Chem.*, 1894, **7**, 47.

[10] See Aloy, *Bull. Soc. chim.*, 1899, [3], **21**, 613.

Uranic Oxide, UO_3, or *Uranyl Oxide*, $(UO_2)O$.—When uranyl nitrate is heated in a glass tube to 250° so long as acid fumes escape, this oxide is left behind in the form of a brownish-yellow powder, whereas, when the nitrate is rapidly decomposed, a red modification of the oxide is produced.[2] It can also be prepared by heating ammonium uranyl carbonate or ammonium uranate in air.

Uranic Hydroxide (*Uranic Acid*), UO_3,H_2O, cannot be obtained by precipitating a uranyl salt by an alkali, the precipitate thus formed consisting of an alkali uranate. It may, however, be prepared, according to Berzelius, by gently calcining the nitrate in a sand-bath as long as nitric acid is evolved. The residue contains uranic hydroxide mixed with a basic salt, which can be removed by washing with boiling water. It may likewise be obtained by evaporating a solution of uranyl nitrate in absolute alcohol, at a moderate heat, until a yellow mass remains, consisting of the hydroxide, $UO_2(OH)_2,H_2O$, or by the electrolysis of uranyl salts at a low current density.[3] This hydrate loses half its water at 80°,[4] or in a vacuum at the ordinary temperature, but at a temperature of 400° it begins to lose oxygen, and is converted into uranoso-uranic oxide, U_3O_8. Uranic hydroxide is yellow, and has a density of 5·92. It does not undergo change in the air, nor does it absorb carbon dioxide.

An orange-coloured hydroxide, UO_3,H_2O, can be obtained by the electrolysis of the nitrate,[5] and is formed in rhombic crystals when the violet hydrate of the oxide U_3O_8 is boiled with water in the air.[6]

This oxide, as mentioned above, yields by the action of acids the *uranyl* salts, whilst with bases it gives rise to the *uranates*. The former have a yellow colour, and most of them possess a remarkable fluorescence,[7] which they impart to glass. The absorption bands exhibited by these compounds have been studied by Becquerel and others. These salts are highly sensitive to light and have been employed for photographic purposes. The most important are described in the sequel, together with the other uranium salts.

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[1] Samsonow, *Kolloid-Zeit.*, 1911, **8**, 96.

[2] Oechsner de Coninck, *Compt. rend.*, 1901, **132**, 204; *Bull. Acad. roy. Belg.*, 1904, 363, 448.

[3] Pierlé, *J. Physical Chem.*, 1919, **23**, 517.

[4] de Forcrand, *Compt. rend.*, 1913, **156**, 1954.

[5] Oechsner de Coninck and Camo, *Bull. Acad. roy. Belg.*, 1901, **8**, 222; Pierlé, *J. Physical Chem.*, 1919, **23**, 517.

[6] Aloy, *Bull. Soc. chim.*, 1900, [3], **23**, 368.

[7] See Trümpler, *Zeit. physikal. Chem.*, 1915, **90**, 385; Bauer, *Schweiz. Chem. Zeit.*, 1918, **2**, 40; Nichols and Howes, *Physical Rev.*, 1919, [2], **14**, 293; Nichols, Howes, and Wick, *ibid.*, 1919, [2], **14**, 201; Nichols and others, *Carnegie Inst. Washington Publication*, 1919, **298**, 1.

The Uranates.—The alkali uranates are obtained by precipitating a uranic salt with an alkali, those of the alkaline earths and other metals by precipitating a mixture of a uranyl salt and a corresponding metallic salt with ammonia. They are also formed when a mixture of a metallic uranate and the acetate or carbonate of the metal is heated in the air. The uranates generally have the composition $M_2O,2UO_3$, and correspond to the dichromates. They are yellow, insoluble in water but soluble in acids, and are decomposed by heat, like uranic oxide itself. Normal uranates are, however, known, as well as potassium and sodium salts of tri-, tetra-, penta-, and hexa-uranic acids.

Potassium Di-uranate, $K_2U_2O_7$.—This is obtained as a pale orange-yellow coloured powder by precipitating a uranyl salt with an excess of potash. Probably the hydroxide is first precipitated and then two molecules unite by the elimination of water, forming uranic acid, which unites with the excess of alkali to form the potassium salt. The *normal* salt can be produced by fusing uranyl chloride with potassium chloride and ammonium chloride, or by heating uranium trioxide with potassium chlorate. Potassium uranate can also be obtained by electrolysis of a neutral solution of potassium uranyl cyanide.[1]

Sodium Di-uranate, $Na_2U_2O_7$, is obtained in a similar manner to the potassium salt, and is known as *uranium yellow*, being used for painting on glass and porcelain, as well as for preparing the yellow glass known as uranium glass. It is prepared on a large scale by roasting 100 parts of pitchblende, containing 45 per cent. of U_3O_8, with 14 parts of lime in a reverberatory furnace. The resulting calcium uranate is treated with dilute sulphuric acid, and the solution of uranic sulphate thus obtained is mixed with sodium carbonate. The uranium is precipitated, together with the other metals, but re-dissolves in an excess of the alkali. On treating this liquid with dilute sulphuric acid, a hydrated sodium uranate, $Na_2U_2O_7,6H_2O$, is obtained.[2]

Ammonium Uranate.—This salt sometimes occurs in commerce as a fine deep yellow-coloured precipitate, termed, like the sodium salt, uranium yellow. It is easily obtained by adding ammonium chloride or sulphate to a boiling solution of sodium uranate, washing the resulting precipitate, and drying at a gentle heat. When heated to redness this salt yields pure uranoso-uranic oxide, and serves therefore as the raw material for the preparation of other uranium compounds.

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[1] Pierlé, *J. Physical Chem.*, 1919, 23, 517.

[2] Patera, *J. pr. Chem.*, 1854, 61, 397.

Uranoso-uranic Oxide or *Green Oxide of Uranium*, $U_3O_8(= UO_2,2UO_3)$, occurs more or less pure in pitchblende. The pure oxide can be obtained by gently heating the trioxide or the dioxide in the air in the form of a satiny, dark-green powder, having density 7·2, and soluble in strong acids. It forms a violet hydroxide which can be prepared by the action of light on a solution of uranyl oxalate or an alcoholic solution of the acetate.[1] A number of violet compounds of uranium are known, being obtained whenever a uranous and a uranic salt are present together at the requisite temperature in neutral or feebly acid medium. By loss of their acid radicles they yield hydrated uranoso-uranic oxide.[2]

Black Oxide of Uranium, or *Uranium Pentoxide*, U_2O_5 $(= UO_2,UO_3)$, is formed when the other oxides, or ammonium uranate, are strongly ignited in the air, and when the nitrate is electrolysed. Zimmermann stated that it possesses no constant composition,[3] but there seems to be no reasonable doubt regarding its individual existence.

An oxide of the composition $U_3O_{10},2H_2O$ is stated to be formed when uranium salts are electrolysed.[4]

Uranium Peroxide, UO_4.—When a very dilute solution of hydrogen peroxide is added to one of uranyl nitrate, a yellowish-white precipitate of peruranic hydroxide, UO_4,xH_2O, is formed, which evolves chlorine when treated with hydrochloric acid.[5] *Peruranates* are formed by the action of alkali and hydrogen peroxide on the uranyl salts (Fairley). Two types of salt are known; in one of these the metal appears to be present as a peroxide and the salt can be hydrolysed by weak acids or bases into a peroxide and uranium peroxide; the hydrolysis of salts of the second type yields uranium peroxide and an ordinary metallic oxide.[6]

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[1] See Aloy, *Bull. Soc. chim.*, 1900, [3], **23**, 368.

[2] Aloy and Rodier, *Bull. Soc. chim.*, 1920, [4], **27**, 101.

[3] *Annalen*, 1886, **232**, 276. See also Lebeau, *Compt. rend.*, 1922, **174**, 388.

[4] Pierlé, *J. Physical Chem.*, 1919, **23**, 517.

[5] Fairley, *Journ. Chem. Soc.*, 1877, i., 127; Hüttig and Schroeder, *Zeit. anorg. Chem.*, 1922, **121**, 243.

[6] Melikoff and Pissarjewsky, *Ber.*, 1897, **30**, 2902; *Zeit. anorg. Chem.*, 1898, **18**, 59; Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 472.

Sodium Peruranate, $(Na_2O_2)_2UO_4,8H_2O$, is precipitated when alcohol is added to a solution of uranyl nitrate, sodium hydroxide, and hydrogen peroxide, and crystallises in golden-yellow needle-shaped crystals, which are somewhat more stable than the potassium salt. If the minimum quantity of caustic soda be employed, a red crystalline salt separates out, having the composition $Na_2O_2(UO_4)_2,6H_2O$. A red, crystalline salt, Na_2UO_5,H_2O, is formed when peruranic hydroxide is added to hydrogen peroxide containing alcohol, sodium hydroxide being then gradually introduced. It slowly decomposes with evolution of oxygen.[1] The formation of a salt of this type is the cause of the red coloration produced when hydrogen peroxide and solid potassium carbonate are added to a uranyl salt.[2]

Lead Peruranate is formed as a double salt with lead uranate, $(PbO)_2UO_4,PbUO_4$, by the action of sodium peruranate on lead acetate. Hydrogen peroxide is liberated in the reaction and the resulting lead salt, when treated with dilute acetic acid, yields lead acetate and peruranic hydroxide, but no hydrogen peroxide (Melikoff and Pissarjewsky). Other salts of the heavy metals are prepared in a similar manner; they are more stable than the corresponding salts of molybdenum and tungsten.

URANIUM AND THE HALOGENS.

507 *Uranium difluoride*, $UF_2,2H_2O$, has been obtained by electrolytic reduction of uranyl chloride in presence of excess of hydrofluoric acid.[3]

Uranium Tetrafluoride or *Uranous Fluoride*, UF_4, is obtained in the form of a voluminous green powder when hydrofluoric acid is added to a solution of uranous chloride. It is insoluble in water and hydrofluoric acid, and when heated in the air it leaves a green residue of oxide. When ignited in hydrogen it loses hydrofluoric acid.[4] The hexahydrate is obtained by electrolysis of potassium uranyl fluoride in acid solution.[5]

Uranous fluoride forms double salts with the alkali fluorides. Potassium urano-fluoride, KF,UF_4, is obtained by the action of reducing agents, such as formic and oxalic acids under the influence of light, upon the potassium urano-oxyfluoride, described below. It is a green powder, resembling uranous fluoride, insoluble in water and in dilute acids.

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[1] Aloy, *Bull. Soc. chim.*, 1903, [3], **29**, 292.
[2] *Ibid.*, **27**, 734.
[3] Giolitti and Agamennone, *Atti R. Accad. Lincei*, 1905, [5], **14**, i., 114, 165.
[4] Carrington Bolton, *Ber. Akad. Wiss. Berlin*, 1866, 299; see also Smithells, *J. Chem. Soc.*, 1883, **43**, 125.
[5] Pierlé, *J. Physical Chem.*, 1919, **23**, 517.

The *hexafluoride* is also known. The reaction between fluorine and uranium is extremely vigorous and the product is mainly the tetrafluoride and small quantities of the hexafluoride, UF_6. The hexafluoride is best prepared from fluorine and the pentachloride cooled in an alcohol and carbon dioxide mixture. It forms glistening, colourless, fuming, monoclinic prisms, which sublime without melting at ordinary temperatures under reduced pressure.[1]

Uranyl Fluoride, UO_2F_2, is a green solid, obtained by the action of hydrofluoric acid on the oxide U_3O_8. It was considered by Smithells[2] to exist in two modifications. It combines with potassium fluoride, yielding *potassium uranyl fluoride*, $UO_2F_2,3KF$, which is a lemon-yellow, crystalline precipitate, and is also formed when an excess of potassium fluoride is added to a solution of uranyl acetate. It is trimorphous (Baker).[3] Corresponding sodium, ammonium, and barium salts are known (Bolton). Hydrogen peroxide converts these salts into deep yellow-coloured peroxyfluorides.[4]

Uranous Oxyfluoride, UOF_2, is formed by the electrolytic or photochemical reduction of uranyl salts.[5]

Uranium Trichloride, UCl_3, is obtained by heating the tetrachloride in hydrogen,[6] or by the continued reduction of uranyl salts with zinc and hydrochloric acid.[7] It is a reddish-brown powder, and dissolves readily in water, forming a red solution, which gradually becomes green with evolution of hydrogen.

Uranium Tetrachloride or *Uranous Chloride*, UCl_4.—This is produced with vivid incandescence, when chlorine is passed over metallic uranium, and is obtained also by igniting uranium dioxide in hydrogen chloride, and, in solution, by exposing a solution of uranic oxide in hydrochloric acid containing alcohol to sunlight;[8] other reduction methods may also be used. It is best prepared by passing chlorine over a heated mixture of charcoal and any of the uranium oxides, or over uranium carbide.[1] Some pentachloride is simultaneously formed, and may be removed by heating the product in a current of carbon dioxide. It can also be prepared by passing carbon tetrachloride over U_3O_8 at a red heat.[2] It crystallises in splendid dark-green octahedra, having a metallic lustre, and volatilising at a red heat to form red vapours with the normal density of 13·3. It is extremely deliquescent, fumes strongly on exposure to the air, and dissolves readily in water, with evolution of heat and formation of a deep emerald-green solution. This, when concentrated in a vacuum, leaves an amorphous, deliquescent mass of uranous chloride, but when evaporated by heat it decomposes, yielding a soluble residue, probably consisting of the oxychloride. Solutions of uranous chloride yield with alkalis a precipitate of uranous hydroxide. The solution acts as a powerful deoxidising agent, reducing gold and silver salts, and converting ferric chloride into ferrous chloride. It was by the analysis of this chloride that Péligot ascertained that the supposed metal was in reality an oxide.

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[1] Ruff, Zedner, Schiller, and Heinzelmann, *Ber.*, 1909, **42**, 492.

[2] *Loc. cit.* See also Giolitti and Agamennone, *loc. cit.*

[3] *Journ. Chem. Soc.*, 1879, **35**, 763.

[4] Lordkipanidzé, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 283.

[5] Giolitti and Agamennone, *Atti R. Accad. Lincei*, 1905, [5], **14**, i., 114, 165.

[6] Péligot, *Ann. Chim. Phys.*, 1842, **5**, 20; Rosenheim and Loebel, *Zeit. anorg. Chem.*, 1908, **57**, 234.

[7] Zimmermann, *Annalen*, 1882, **213**, 320.

[8] Aloy, *Bull. Soc. chim.*, 1899, [3], **21**, 613; Aloy and Rodier, *ibid.*, 1922, [4], **31**, 246.

Uranium tetrachloride combines directly with ammonia, forming the compound $3UCl_4,4NH_3$, and unites with the heated chlorides of potassium, lithium, and the metals of the calcium group, forming green salts, $UCl_4,2M^{I}Cl$ or $UCl_4,M^{II}Cl_2$, which are decomposed by water (Aloy).

Benrath[3] considers that the greenish-yellow powder deposited when uranyl chloride dissolved in ether is exposed to sunlight is the *oxychloride*, $UOCl_2$.

Uranium Pentachloride, UCl_5, is obtained by the direct union of the tetrachloride with chlorine. It exists in two distinct forms, according as it is produced slowly or quickly. When the current of chlorine is slow, the uranium pentachloride forms long, dark, needle-shaped crystals, which reflect light with a green, metallic lustre, but are of a splendid ruby-red colour when viewed by transmitted light. If the rate at which the chlorine passes be rapid, the pentachloride is deposited in the form of a light brown, mobile powder. Both forms are hygroscopic, yielding yellowish-green liquids on exposure to the air for a few minutes, and hissing and giving off fumes of hydrochloric acid when thrown into water. Uranium pentachloride cannot be volatilised without partial decomposition, since uranium tetrachloride and free chlorine are formed. The tetrachloride when similarly heated loses no chlorine.[1] There are reasons for regarding uranium pentachloride as possessing the constitution $UCl_4 \cdot UCl_6$. The free hexachloride is not, however, known.

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[1] Aloy, *Bull. Soc. chim.*, 1899, [3], 21, 264; Roderburg, *Zeit. anorg. Chem.*, 1913, 81, 122; Lely and Hamburger, *ibid.*, 1914, 87, 209; Rideal, *J. Soc. Chem. Ind.*, 1914, 33, 673.

[2] Colani, *Ann. Chim. Phys.*, 1907, [8], 12, 59.

[3] *Zeit. wiss. Photochem.*, 1917, 16, 253.

Uranyl Chloride or *Uranium Oxychloride*, UO_2Cl_2, is formed when dry chlorine gas is passed over uranium dioxide at a red heat. The tube then becomes filled with the orange-yellow vapour of this compound, which solidifies to a yellow, crystalline mass, and is easily fusible, but not very volatile. When strongly heated in dry air, it yields chlorine and the dioxide, which then becomes oxidised.[2]

Uranyl chloride is soluble in water, alcohol, or ether, and its aqueous solution yields on evaporation crystals of the hydrate, UO_2Cl_2,H_2O. This may be obtained in solution by acting upon uranic oxide with hydrochloric acid, or by oxidising a solution of uranous chloride with nitric acid.[3]

Uranyl chloride forms double chlorides with the chlorides of the alkali metals. The ammonium salt, $2NH_4Cl,UO_2Cl_2,2H_2O$, crystallises in rhombohedra from a syrupy solution of the mixed salts. The potassium salt, $2KCl,UO_2Cl_2,2H_2O$, is obtained by dissolving potassium uranate in excess of hydrochloric acid, adding potassium chloride, and evaporating, when large, rhombic tablets separate out, which have a yellowish-green colour, and are very soluble.[4] The anhydrous compound can be obtained by passing the vapour of the oxychloride over heated potassium chloride.[5] Uranyl chloride combines also with the hydrochlorides of the organic bases (Greville Williams). Several basic chlorides have been described.[6]

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[1] Roscoe, *Journ. Chem. Soc.*, 1874, 933; Ruff and Heinzelmann, *Ber.*, 1909, **42**, 492; *Zeit. anorg. Chem.*, 1911, **72**, 63; Camboulives, *Compt. rend.*, 1910, **150**, 175.

[2] Oechsner de Coninck, *Ann. Chim. Phys.*, 1904, [8], **3**, 500.

[3] See Mylius and Dietz, *Ber.*, 1901, **34**, 2774.

[4] See Rimbach, *Ber.*, 1904, **37**, 461.

[5] Aloy, *Bull. Soc. chim.*, 1901, [3], **25**, 153.

[6] *Ibid.*, 1899, [3], **21**, 613; Orloff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 375; 1903, **35**, 513.

Uranium Tribromide, UBr_3, has been described as dark brown needles.[1]

Uranium Tetrabromide, UBr_4, is obtained by heating in an atmosphere of bromine vapour a previously ignited mixture of uranous oxide and six times its weight of starch, or of the green oxide with sugar charcoal.[2] The bromide is deposited in the more strongly-heated portions of the tube in lustrous brown tablets of density 4·838 at 21°/4°. The density of its vapour is 19·5. It loses its lustre and becomes dull yellow on the surface in the presence of even traces of oxygen, fumes in the air, and is very deliquescent.

Uranyl Bromide or *Uranium Oxybromide*, UO_2Br_2, is obtained by treating uranous oxide with bromine and water, or by dissolving uranic oxide in hydrobromic acid. On evaporation, yellow needles are deposited, which have a styptic taste and decompose when heated.[3]

Uranium Tetraiodide, UI_4, described by Rammelsberg, is obtained by dissolving uranous hydroxide in hydriodic acid. A green solution is thus formed which decomposes on evaporation. The solid substance is formed as a crystalline sublimate when iodine vapour is passed over uranium at a temperature of 500° in sealed vacuum tubes. It forms black needles melting at 500°, and dissolves in water, giving a green acid solution.[4]

Uranyl Iodide, UO_2I_2, is formed when a slight excess of barium iodide is added to an ethereal solution of the nitrate, and separates in red, deliquescent, unstable crystals.[5]

Uranyl chlorate, perchlorate, and *iodate,* and double compounds of the last-named with potassium iodate, have been described.

URANIUM AND SULPHUR.

508 *Uranium Sesquisulphide*, U_2S_3, is prepared by heating UBr_3 in hydrogen sulphide, and yields *uranium monosulphide*, US, when heated in hydrogen.[6]

Uranous Sulphide, US_2, is obtained, according to Péligot, when metallic uranium is heated in sulphur vapour. The mass takes fire and an amorphous, greyish-black powder is obtained which becomes crystalline when ignited in absence of air. It may also be formed by passing a carefully dried mixture of hydrogen and sulphur vapour over sodium uranium chloride. The sulphide is thus obtained in small, flattened crystals.[1]

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[1] Alibegoff, *Annalen*, 1882, 233, 104, 131, 135.

[2] Richards and Merigold, *Zeit. anorg. Chem.*, 1902, 31, 250.

[3] See Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1902, 12, 1025.

[4] Guichard, *Compt. rend.*, 1907, 145, 921.

[5] Aloy, *Ann. Chim. Phys.*, 1901, [7], 24, 412.

[6] Alibegoff, *Annalen*, 1886, 233, 117.

Ammonium sulphide always gives a black precipitate of the hydrated sulphide with uranous salts. In moist air it loses hydrogen sulphide and forms uranyl sulphide, UO_2S.

An *oxysulphide*, UOS, is obtained when UO_2,U_3O_8 or ammonium uranate is heated in hydrogen sulphide.

Uranyl Sulphide, UO_2S, is precipitated when ammonium sulphide is added to a solution of uranyl nitrate. It oxidises quickly on exposure to air, and dissolves easily in acids and in ammonium carbonate. When heated in the presence of water until all the ammonium sulphide has been driven off, it decomposes into sulphur and the dioxide. If air be excluded the ammonium sulphide acts as a reducing agent,[2] and the residual black powder has the composition U_7O_{16}. Uranyl sulphide is formed in black, needle-shaped, tetragonal crystals when the green oxide is strongly heated with potassium thiocyanate and sulphur.[3]

Uranium Red.—When hydrogen sulphide is passed into a solution of uranyl nitrate to which about 2·8 molecular proportions of potassium hydroxide have been added, an orange-yellow precipitate is produced which dries to a hard, amorphous, brick-red mass and has the composition $5UO_3,2K_2O,H_2S_2$. When this substance is treated with potassium carbonate or hydroxide it is converted into uranium red, which is a blood-red precipitate and dries to a brittle, amorphous mass resembling potassium permanganate in appearance and yielding a carmine-red powder. This compound has not been obtained free from water, but has the composition $5UO_3,2K_2O,HS_2K,xH_2O$, and is converted into the orange-yellow substance by carbonic acid. Acids decompose it with liberation of half the sulphur as free sulphur and half as hydrogen sulphide.[4] An analogous ammonium-red can be obtained by the action of ammonium sulphide on uranyl nitrate, and it was in this way that uranium red was first prepared.[5]

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[1] Colani, *Ann. Chim. Phys.*, 1907, [8], **12**, 59.

[2] For conditions of formation of uranous sulphide, see Wilke-Dörfurt, *Chem. Zentr.*, 1921, i., 170.

[3] Milbauer, *Zeit. anorg. Chem.*, 1904, **42**, 448.

[4] Kohlschütter, *Annalen*, 1900, **314**, 311.

[5] Patera, *J. pr. Chem.*, 1850, **51**, 122; Remelé, *Annalen*, 1865, **135**, 209; Zimmermann, *ibid.*, 1880, **204**, 204.

The *selenides*, USe_2 and U_2Se_3, and the *telluride*, U_2Te_3, have been obtained in the crystalline state by heating the double chloride, $UCl_4,2NaCl$, in hydrogen containing the vapour of selenium or tellurium.[1] A crystalline *uranyl selenide*, UO_2Se, is obtained by heating the green oxide with potassium cyanide and sulphur.[2]

Uranyl Sulphite.—When sulphur dioxide is passed into a solution of uranyl acetate, a crystalline precipitate is produced which has the empirical composition $UO_3{\cdot}SO_2,4H_2O$ and was regarded by Girard[3] as the normal sulphite, $UO_2{\cdot}SO_3,4H_2O$. Kohlschütter,[4] however, formulates it as a uranyl sulphurous acid, $SO_3H{\cdot}UO_2{\cdot}OH,3H_2O$, and has prepared a number of complex alkali salts. A basic *uranous sulphite*, $UO{\cdot}SO_3,2H_2O$, is also believed to exist.

Uranous Sulphate, $U(SO_4)_2,9H_2O$, crystallises from aqueous solution in greenish, monoclinic, twinned prisms and is isomorphous with crystallised thorium sulphate.[5] It is, however, usually obtained with $8H_2O$. In order to prepare this salt, the green oxide, U_3O_8, is dissolved in dilute sulphuric acid and the solution allowed to crystallise after addition of some alcohol. The mother-liquor, which contains uranyl sulphate, yields another crop of crystals of uranous sulphate after it has remained exposed to the light, inasmuch as the uranyl salt present in solution is reduced by the alcohol.

Sodium thiosulphate has also been found a satisfactory reducing agent. Uranous sulphate forms a stable hydrate with $4H_2O$ and several other hydrates, and is readily decomposed by water with formation of basic salts.[6] It forms double salts with the sulphates of the alkali metals;[7] as, for instance, $U(SO_4)_2,K_2SO_4,2H_2O$, and $U(SO_4)_2,4(NH_4)_2SO_4,3H_2O$.

An *acid uranium sulphate*, $(USO_4)_2H$, containing tervalent uranium, has been obtained by an electrolytic method.[8]

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[1] Colani, *Compt. rend.*, 1903, **137**, 382.

[2] Milbauer, *Zeit. anorg. Chem.*, 1904, **42**, 450.

[3] *Compt. rend.*, 1852, **34**, 22.

[4] *Annalen*, 1900, **311**, 1.

[5] Rammelsberg, *Zeit. Kryst. Min.*, 1889, **15**, 640. For a general discussion of the relation of uranous salts to those of thorium, see Fleck, *J. Chem. Soc.*, 1914, **105**, 247.

[6] Orloff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 381; Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1901, 483; Kohlschütter, *Ber.*, 1901, **34**, 3628; Giolitti and Bucci, *Gazz.*, 1905, **35**, ii., 151, 162; Giolitti and Liberi, *ibid.*, 1906, **36**, ii., 443.

[7] See Kohlschütter, *Ber.*, 1901, **34**, 3619.

[8] Rosenheim and Loebel, *Zeit. anorg. Chem.*, 1908, **57**, 234.

Uranyl Sulphate, $UO_2 \cdot SO_4, 3H_2O$, is obtained by heating uranyl nitrate with sulphuric acid, and does not crystallise readily. It dissolves in about 20 parts of water at the ordinary temperature.[1] When dissolved in moderately concentrated sulphuric acid, fine, yellowish-green, fluorescent crystals of $UO_2 \cdot SO_4, H_2SO_4$ are deposited on cooling, whilst from a solution in concentrated sulphuric acid crystals of a disulphate, $UO_2 \cdot S_2O_7$, are deposited, which do not fluoresce. By the gradual oxidation of the pitchblende found in Joachimsthal, several new uranium minerals have been formed. Amongst the more important are certain sulphates, such as uranium-vitriol or johannite, and some basic sulphates.

Uranyl sulphate forms double salts with the sulphates of the alkali metals, such as $UO_2 \cdot SO_4, K_2SO_4, 2H_2O$. This is very soluble, and crystallises in yellow crusts, whilst the sparingly soluble ammonium salt, $UO_2 \cdot SO_4, (NH_4)_2SO_4, 2H_2O$, is deposited in monoclinic, lemon-coloured prisms.[2]

Uranyl *selenite, selenate, chromates, molybdates*, and *tungstates* have been studied, and their existence has been confirmed.

URANIUM AND NITROGEN, PHOSPHORUS, ARSENIC, AND BORON.

509 *Uranium Nitride.*—Uranium combines directly with nitrogen at 1000°, forming a yellow nitride,[3] the composition of which is not stated. The *nitride*, U_3N_4, is obtained as a grey or black powder by heating the tetrachloride in ammonia, mixing the product with ammonium chloride, and again igniting in an atmosphere of ammonia.[4]

Uranyl Nitrate, $UO_2(NO_3)_2, 6H_2O$.—This salt, which is commonly known as uranium nitrate, is prepared by dissolving any of the oxides of uranium in nitric acid. It crystallises in fine, lemon-yellow, fluorescent, rhombic[5] prisms, which are soluble in half their weight of water[6] and deliquesce on exposure. Icositetra-, tri-, di-, and mono-hydrates and the anhydrous salt are known to exist.[1] The aqueous solution has an acid reaction owing to the partial hydrolysis of the salt.[2] The nitrate is prepared commercially by igniting ammonium uranate, $(NH_4)_2U_2O_7$, and dissolving the oxide in nitric acid.[3] When crystals of uranyl nitrate are shaken or ground together, triboluminescence (emission of light under such conditions) is observed. The explosive property of uranyl nitrate, which has in these circumstances frequently been observed, is apparently not an inherent property of the salt, but is attributed to the presence of an unstable compound produced when nitric acid is present during its recrystallisation from ether.[4] Uranyl nitrate readily forms double salts with the alkali nitrates.[5]

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[1] Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1901, 222, 349; 1902, 94, 161.

[2] See also Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1904, 1171; 1905, 50, 94, 161, 182.

[3] Moissan, *Compt. rend.*, 1896, **122**, 274.

[4] Kohlschütter, *Annalen*, 1901, **317**, 158. See also Colani, *Compt. rend.*, 1903, **137**, 382; Haber and Greenwood, *Zeit. Elektrochem.*, 1915, **21**, 241; Ger. Pat. 229126.

[5] See, however, Quercigh, *Riv. min. crist. Ital.*, 1915, **44**, 6.

[6] See Oechsner de Coninck, *Compt. rend.*, 1900, **131**, 1219, 1303; 1901, **132**, 90, 204; *Bull. Acad. roy. Belg.*, 1901, 222; *Bull. Soc. chim.*, 1915, [4], **17**, 422.

Uranium phosphide, U_3P_4, *arsenide*, U_3As_4, and *antimonide*, U_3Sb_4, have been prepared by Colani[6] in a similar manner to the telluride as black, crystalline powders, readily oxidised by nitric acid.

Uranyl hypophosphite, $UO_2(H_2PO_2)_2$, and complex alkali salts have also been prepared.[7]

Uranous metaphosphate, $U(PO_3)_4$, *uranous pyrophosphate*, UP_2O_7, and *uranous orthophosphate*, $U_3(PO_4)_4$, have been prepared by Colani,[8] as well as complex salts with alkali- and alkaline earth-metal phosphates.

Uranyl Phosphates.—The normal orthophosphate is not known. The mono-hydrogen salt, $H(UO_2)PO_4,4H_2O$, is deposited in yellow, tetragonal plates from a solution of precipitated uranium phosphate in hot water acidified with hydrochloric acid.[9] When uranic oxide is treated with phosphoric acid, a crystalline powder is obtained which is partially soluble in water, and the solution deposits yellow crystals of the di-hydrogen salt,

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[1] de Forcrand, *Compt. rend.*, 1913, **156**, 1044, 1207; *Ann. Chim.*, 1915, [9], **3**, 5; Gormann, *J. Amer. Chem. Soc.*, 1922, **44**, 1466.

[2] Ley, *Zeit. physikal. Chem.*, 1899, **30**, 193; *Ber.*, 1900, **33**, 2658; Dittrich, *Zeit. physikal. Chem.*, 1899, **29**, 449. See also Gomez, *Anal. Fis. Quim.*, 1919, **17**, 24.

[3] Janda, *Oester. Zeit. Berg.-Hutt.*, 1901, **49**, 325.

[4] Ivanov, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 078; *Chem. Zeit.*, 1912, **36**, 297, 499; Andrews, *ibid.*, 1912, **36**, 1463; *J. Amer. Chem. Soc.*, 1912, **34**, 1686; Eichhorn, *Chem. Zeit.*, 1914, **38**, 139; Müller, *ibid.*, 1916, **40**, 38; 1917, **41**, 439; Siemssen, *ibid.*, 1919, **43**, 267; *ibid.*, 1922, **46**, 450.

[5] Meyer and Wendel, *Ber.*, 1903, **36**, 4055; Rimbach, *ibid.*, 1904, **37**, 461.

[6] *Compt. rend.*, 1903, **137**, 382.

[7] Rosenheim and Trewendt, *Ber.*, 1922, **55**, [*B*], 1957.

[8] *Ann. Chim. Phys.*, 1907, [8], **12**, 59.

[9] Bourgeois, *Bull. Soc. franç. Min.*, 1898, **21**, 32.

$UO_2(H_2PO_4)_2,3H_2O$. Both the *pyrophosphate* and the *metaphosphate* have been described.

Uranyl Ammonium Phosphate, $UO_2NH_4PO_4$, is a greenish-yellow precipitate, insoluble in acetic acid, obtained by adding a soluble phosphate to a solution of uranyl acetate containing ammonium chloride. This reaction is employed for the volumetric estimation of uranium, or of phosphoric acid.

Uranyl Arsenates.—Several of these compounds exist as minerals (Winkler). Trögerite has the composition $(UO_2)_3(AsO_4)_2,12H_2O$; walpurgite is a basic arsenate of uranyl and bismuth; uranospinite is an arsenate of uranium and calcium. Various simple and complex arsenates have been prepared artificially.

Uranium Boride, UB_2.—When an electric arc is produced between electrodes of compressed powdered boron and uranium, a boride, UB_2, is formed, having a metallic appearance. It is stable towards alkalis and acids with the exception of a nitric–hydrofluoric acid mixture, but is readily attacked by fused alkali hydroxide.[1]

URANIUM AND CARBON.

510 *Uranium Carbide*, UC_2, is obtained by strongly heating a mixture of 500 grams of green uranium oxide and 60 grams of charcoal in the electric furnace, and is a crystalline, lustrous solid, which scratches rock crystal but not corundum, and has a density of 11·28 at 18°. It was considered by Moissan to possess the formula U_2C_3. It is attacked by fluorine when gently warmed, by chlorine at 350°, and by oxygen at 370°. In contact with water, about one-third of the carbon is evolved as a gaseous mixture containing 0·2–0·7 per cent. of acetylene, 5·0–7·0 per cent. of ethylene, 78–81 per cent. of methane, and 13·5–15·0 per cent. of hydrogen, the remainder of the carbon being converted into a mixture of solid and liquid hydrocarbons.[2] When two pieces of the carbide are rubbed together, or even shaken in a bottle, brilliant sparks are given off.

Uranyl Carbonates.—Double salts of uranyl carbonate and alkali carbonates are obtained by precipitating a uranyl salt with an alkali carbonate. The potassium salt, $UO_2 \cdot CO_3,2K_2CO_3$, is obtained by dissolving potassium uranate in potassium bicarbonate, and evaporating at a moderate temperature, when the compound is deposited in silky, crystalline crusts.[1] Water dissolves at the ordinary temperature 7 per cent. of its weight of this salt. The corresponding sodium salt is obtained in a similar way, and possesses similar properties. The ammonium compound, $UO_2 \cdot CO_3,2(NH_4)_2CO_3$, is prepared by gently warming ammonium uranate with a solution of ammonium carbonate, and separates out on cooling in lemon-yellow, small, flat, monoclinic prisms. It dissolves at the ordinary temperature in 20 per cent. of water, but is less soluble in water containing ammonium carbonate. The mineral liebigite is a uranyl calcium carbonate, $UO_2 \cdot CO_3,CaCO_3,10H_2O$, which occurs as an apple-green, warty mass, together with other uranium minerals.

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[1] Wedekind, *Ber.*, 1913, **46**, 1198.

[2] Moissan, *Compt. rend.*, 1896, **122**, 274; Lebeau, *Compt. rend.*, 1911, **152**, 955; *Bull. Soc. chim.*, 1911, [4], **9**, 512; Lebeau and Damiens, *Compt. rend.*, 1913, **156**, 1987; Polushkin, *Iron and Steel Inst., Carnegie Schol. Mem.*, 1920, **10**, 129.

Cyanides, etc.—Potassium uranyl cyanide,[2] $K_2[UO_2(CN)_4]$, uranyl cyanate,[3] $UO_2(CNO)_2$, and its complex salts, and uranyl thiocyanates,[4] $UO_2(CNS)_2,8H_2O$, and its double salts have been described.

Organic Complexes.—Complexes with formic, acetic, oxalic, and a number of other organic acids have been studied.[5]

Uranium Silicide, USi_2, has been prepared by an aluminothermic method. It is a grey, lustrous powder which is not easily attacked by oxygen.[6]

DETECTION AND ESTIMATION OF URANIUM.

511 The uranous salts are green and pass rapidly by oxidation into the uranyl salts, which have a yellow colour, and yield with alkalis or alkali carbonates yellow precipitates of the alkali uranates. Although uranyl salts do not give precipitates with cupferron (nitrosophenylhydroxylamine), uranous salts are completely precipitated by this reagent.[7] Uranyl salts with ammonium sulphide yield a brown precipitate of uranyl sulphide,

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[1] See also Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1904, 363, 448.

[2] Aloy, *Ann. Chim. Phys.*, 1901, [7], **24**, 412.

[3] Pascal, *Bull. Soc. chim.*, 1914, [5], **15**, 11.

[4] Pascal, *Compt. rend.*, 1914, **158**, 1672.

[5] For recent work, see Mazzucchelli and d'Alceo, *Atti R. Accad. Lincei*, 1912, [5], **21**, ii., 620, 850; 1913, [5], **22**, i., 41; Courtois, *Compt rend.*, 1914, **158**, 1511, 1688; Henri and Landau, *ibid.*, 1914, **158**, 181; Mazzucchelli and Sabatini, *Gazz.*, 1915, **45**, [2], 225; Bauer, *Schweiz. Chem. Zeit.*, 1918, **2**, 40; Hatt, *Zeit. physikal. Chem.*, 1918, **92**, 513.

[6] Defacqz, *Compt. rend.*, 1908, **147**, 1050.

[7] Auger, *Compt. rend.*, 1920, **170**, 995. See also Browning, *J. Amer. Chem. Soc.*, 1921, **43**, 114.

UO_2S, soluble in dilute acids and in ammonium carbonate; potassium ferrocyanide also yields a brown precipitate. In the absence of sulphuric or hydrochloric acid, uranium compounds in nitric acid solution yield, after the addition of excess of zinc, a yellow deposit on the metal, consisting of the hydrated trioxide.[1]

In the general separation of the metals, uranium is obtained together with iron. In order to separate these, advantage is taken of the solubility of uranium oxide and uranates in ammonium carbonate solution, a complex ammonium uranyl carbonate being formed. When a uranium compound is fused with microcosmic salt in the oxidising flame, a yellow bead is obtained which on cooling becomes green, and on re-heating attains a darker green colour. In the reducing flame, the bead is green.

Most of the uranyl salts show a strong fluorescence, and give a characteristic absorption spectrum, which has been examined by Morton and Bolton,[2] whilst the fluorescence and phosphorescence spectra have been described by E. Becquerel[3] and H. Becquerel.[4]

The uranium compounds do not impart any tint to the non-luminous gas flame. The spark spectrum of uranium is a complicated one, and has been mapped by Thalen. It consists of a large number of lines, of which five in the green are conspicuous by their brightness, viz., 5495, 5482, 5480, 5478, and 5475; there are also three specially bright lines in the more refrangible portions, viz., 4473, 4363, and 4341.[5]

In order to estimate uranium it is precipitated as uranyl ammonium phosphate and weighed finally as uranyl pyrophosphate, $(UO_2)_2P_2O_7$, or it is converted into a uranyl salt, precipitated with ammonia,[6] and the washed precipitate converted by ignition in hydrogen into the brown oxide, UO_2. Small quantities may be estimated colorimetrically by comparison of the red coloration obtained when a uranyl salt is treated with sodium salicylate.[1] Further, it may, like iron, be estimated volumetrically with a solution of potassium permanganate, the uranyl compound being previously reduced to the uranous state by the action of zinc and sulphuric acid, or of titanous sulphate,[2] or a solution of uranyl acetate may be titrated with sodium phosphate.

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[1] Buell, *J. Ind. Eng. Chem.*, 1922, **14**, 593.

[2] *American Chemist*, **3**, 360, 401. See also Vogel, *Ber.*, 1875, **8**, 1535; 1878, **11**, 915; Zimmermann, *Annalen*, 1882, **215**, 285; Mazzucchelli and Perret, *Atti R. Accad. Lincei*, 1913, [5], **22**, ii., 445.

[3] *Compt. rend.*, 1872, **75**; 1879, **88**, 1237.

[4] *Ibid.*, 1885, **101**, 1252; 1907, **144**, 459.

[5] See also Exner and Haschek, "*Die Spektren der Elemente bei normalem Druck*," Leipzig, 1911; Siegbahn and Friman, *Physikal. Zeit.*, 1916, **17**, 17, 61; *Phil. Mag.*, 1916, [6], **31**, 403; 1916, [6], **32**, 39; Siegbahn, *Ber. deut. physikal. Ges.*, 1916, **18**, 150; Dauvillier, *Compt. rend.*, 1921, **172**, 1350; Moir, *Trans. Roy. Soc. South Africa*, 1921, **10**, 33.

[6] Schwarz, *Helv. Chim. Acta*, 1920, **3**, 330. A summary of the best methods is also given by Kern, *J. Amer. Chem. Soc.*, 1901, **23**, 685. Recent papers on the subject are: König, *Chem. Zeit.*, 1913, **37**, 1106; Wunder and Wenger, *Zeit. anal. Chem.*, 1914, **53**, 371; Turner, *Amer. J. Sci.*, 1916, [4], **42**, 109; Scholl, *J. Ind. Eng. Chem.*, 1919, **11**, 842; Pierlé, *ibid.*, 1920, **12**, 60.

The *Atomic Weight* of uranium was determined by Péligot by the analysis of the tetrachloride, which he found to contain 37·2 per cent. of chlorine, whence he calculated the atomic weight to be 237·6. He afterwards obtained the number 238·3 by the conversion of the acetate, $UO_2(C_2H_3O_2)_2,H_2O$, into the dioxide. Zimmermann, on the other hand, by the same method, obtained the number 237·7, whilst from a series of experiments in which he converted the dioxide into the green oxide and *vice versa* the number 237·8 was found.[3] Aloy,[4] by the determination of the ratio $UO_2 : N$ in pure uranyl nitrate, obtained the value 237·6 ($N = 13{\cdot}93$), which becomes 237·1 when the more modern value $N = 13{\cdot}90$ is adopted. Richards and Merigold,[5] by analysis of the very carefully purified tribromide, obtained the value 238·5, whilst Lebeau[6] found the same number by the reduction of uranyl nitrate dihydrate to uranium oxide by heating the salt in a current of hydrogen to 1100°. Oechsner de Coninck,[7] by igniting uranyl oxalate to the dioxide, obtained the value 238·4; that of Hönigschmid,[8] by the conversion of the tetrabromide to silver bromide, was 238·175. Hönigschmid and Horovitz,[9] by determinations of the same ratio, obtained an atomic weight of 238·043 ± 0·018 when the tetrabromide was finally sublimed in bromine vapour, and 238·159 ± 0·023 when it was finally sublimed in nitrogen. The actual atomic weight appears, therefore, to be not higher than 238·2; hence this number is now (1922) adopted.

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[1] Müller, *Chem. Zeit.*, 1919, **43**, 739.

[2] Newton and Hughes, *J. Amer. Chem. Soc.*, 1915, **37**, 1711.

[3] *Annalen*, 1886, **213**, 299.

[4] *Compt. rend.*, 1901, **132**, 551.

[5] *Zeit. anorg. Chem.*, 1902, **31**, 235.

[6] *Compt. rend.*, 1912, **155**, 163.

[7] *Ibid.*, 1511.

[8] *Ibid.*, 1914, **158**, 2004.

[9] *Monatsh.*, 1916, **37**, 185.

GROUP VII.

Sub-group (*a*)	*Sub-group* (*b*)
Manganese.	Fluorine. Chlorine. Bromine. Iodine.

512 In the periodic system, manganese is the only representative of the even series of the seventh group known.

The halogen elements have already been described in Vol. I. The analogy of manganese with these elements is almost entirely confined to the derivatives of its highest oxide, Mn_2O_7. To this oxide corresponds permanganic acid, $HMnO_4$, the salts of which are isomorphous with the perchlorates.

In its general behaviour, however, manganese shows strong resemblances to chromium, iron, and its neighbours in the same horizontal series of the periodic table:

Group.	IV.	V.	VI.	VII.	VIII.	I.	II.
Element	Ti	V	Cr	Mn	(Fe Co Ni)	Cu	Zn

Manganese, titanium, vanadium, chromium, iron, cobalt, and nickel are all hard, white metals of high melting point. Manganese, iron, cobalt, and nickel, or their alloys, have strong magnetic properties. The whole of the elements in the above series have a great tendency to form double or complex salts.

They all form oxides of the type RO, and a series of salts in which the metal is divalent; many examples of isomorphism between manganous and the corresponding ferrous, cobaltous, nickelous, cupric, and zinc compounds are known, but our knowledge of the divalent compounds of titanium, vanadium, and chromium is slight.

With the exception of copper and zinc, all these elements form an oxide of the type R_2O_3 and salts in which they are trivalent, a well-known isomorphous series being the alums which are formed by titanium, vanadium, chromium, manganese, iron, and cobalt. Manganese, like chromium and iron, forms mixed oxides with other elements of the type RO,Mn_2O_3; it also forms an oxide, Mn_3O_4 or MnO,Mn_2O_3, analogous to the similar compounds of iron, cobalt and nickel.

Manganese has a dioxide, MnO_2, isomorphous with rutile, TiO_2; vanadium, chromium, cobalt, and nickel also form dioxides, all of which, except the chromium compound, can act as weak acidic oxides and form manganites (*e.g.*, $CaMnO_3$), titanates, vanadites, cobaltites, and nickelites. Though iron dioxide is unknown, corresponding compounds (*e.g.*, $BaFeO_3$) are known. The dioxides of manganese, titanium, and vanadium can also act as basic oxides, and give rise to a series of salts in which the metals are tetravalent.

Manganese, like chromium, has a trioxide, MnO_3, which is a purely acidic oxide and forms manganates (*e.g.*, K_2MnO_4), which are isomorphous with the corresponding chromates and ferrates.

MANGANESE. Mn = 54·93. At. No. 25.

513 Black oxide of manganese, manganese dioxide, or pyrolusite was known in early times, but for a long period this compound was confounded with magnetic iron ore, and this fact explains the statement of Pliny that loadstone was employed in the manufacture of glass for the purpose of removing or attracting the impurities of colouring matters out of the glass. He distinguished, moreover, special kinds of magnes; one of these, which is of the feminine gender, does not attract iron: "magnes qui niger est et feminei sexus, ideoque sine viribus." This probably was manganese dioxide. The derivation of the word magnet appears to be doubtful. In the Middle Ages loadstone was distinguished as *magnes* or *magnesius lapis*. Pyrolusite, however, was termed *magnesia* probably because Pliny had already pointed out the existence of two species of loadstone. Many of the alchemists, however, believed it to be an ore of iron. They likewise mention its use in glass-making, and in the Latin manuscripts of the sixteenth century it is termed *lapis manganensis*, or some similar name.

In 1740, Pott, in his treatise entitled "*Examen chymicum magnesia vitrariorum, Germanis Braunstein*," proved that the black oxide of manganese did not contain iron, and that from it a definite series of salts could be obtained. He did not, however, suggest that it contained a new metal. Scheele's celebrated investigations on manganese were published in the year 1774. In these he showed that the mineral manganese possesses a strong attraction for phlogiston, and that it takes this substance up, uniting with acids to form colourless salts, this being explained, according to our present views, by the fact that it gives off oxygen. On the other hand, the solutions of manganese which did not contain phlogiston were shown to be coloured. Scheele believed that the earth contained in this mineral resembled lime; but in the above-mentioned year Bergman, founding his deductions upon Scheele's experiments, came to the conclusion that manganese was probably the calx of a new metal, inasmuch as it coloured glass, and its solutions were precipitated by prussiate of potash, these being reactions common to the metallic calces. Gahn was, however, the first to isolate the new metal. In Germany, this was called braunstein-könig or braunstein-metal. In other languages, in which braunstein was termed *magnesia niger*, in order to distinguish it from *magnesia alba*, the metal was called manganese or manganesium.

Manganese occurs in nature chiefly as the dioxide or pyrolusite, MnO_2. It is found also in the following minerals: braunite, Mn_2O_3; hausmannite, Mn_3O_4; psilomelane, $(Mn,Ba)O,MnO_2$; manganite, Mn_2O_3,H_2O; rhodocrosite or manganese spar, $MnCO_3$, which also frequently occurs as an isomorphous constituent in ferrous carbonate and other similar minerals. Manganese occurs also as alabandite or sulphide of manganese, MnS; and hauerite, or manganese disulphide, MnS_2. It likewise forms an essential constituent of many other minerals, although occurring in them only in small quantity. Thus, for instance, most silicates contain manganese, which frequently imparts to them their peculiar colour. By means of these minerals the metal manganese passes into the soil and into drainage water, whence it is absorbed in small quantities into the bodies of plants and animals.

The natural oxides of manganese usually contain traces of potassium, rubidium, silver, and copper, whilst gallium, indium, and thallium are occasionally present.[1]

514 *Preparation of Metallic Manganese.*—The higher oxides of manganese can be reduced only to manganese monoxide at a red heat, the metal not being formed either when the oxide is heated alone or mixed with charcoal in a current of hydrogen until the temperature rises to white heat. The original method of preparing the metal, proposed by John,[2] depends upon this fact. Finely divided oxide of manganese, obtained by the

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[1] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, 71, 533.

[2] Gehlen's *Journ. Chem. Phys.*, 3, 452.

calcination of the carbonate in a covered crucible, is well mixed with carbon, and the mixture formed into a paste with oil; the paste is then introduced into a crucible lined with charcoal, and the upper portion completely filled with powdered charcoal. The crucible is first heated to redness for half-an-hour to solidfy the mass, after which the cover is carefully luted down, and the whole exposed to a wind furnace for an hour-and-a-half to the highest temperature which the crucible can support without fusing. The regulus thus prepared contains both carbon and silicon derived from the ashes of the wood charcoal. By igniting the metal a second time in a charcoal crucible with some borax it was obtained by John in a more fusible and brilliant state, and so free from carbon that it left no black residue when treated with an acid.

Deville's method[1] consists in mixing red manganese oxide, Mn_3O_4, prepared by heating the artificial dioxide, with sugar charcoal insufficient in quantity for complete reduction. The mixture is heated to whiteness in a doubly-lined crucible. The regulus obtained is coated with a violet, crystalline mass, apparently calcium-manganese spinel, CaO,Mn_2O_3.

Jordan[2] describes a method of preparing metallic manganese on a large scale by treating manganese ores in a blast furnace. The metal obtained is really ferro-manganese, containing 85 per cent. of manganese, 6 per cent. of carbon, 8 per cent. of iron, and traces of silicon, sulphur, and phosphorus.

Other processes of preparing the metal consist in igniting a mixture of fluor-spar and chloride of manganese with metallic sodium,[3] or gradually adding 15 grams of metallic magnesium to a fused mixture of 100 grams of manganese chloride and 200 grams of potassium chloride.[4] The metal may be obtained also by the electrolysis of a concentrated solution of the chloride according to the process described by Bunsen,[5] or by heating the amalgam, which can be prepared electrolytically.[6]

The method of reducing manganese oxide by aluminium is due to Greene and Wahl,[7] who devised it for producing the pure metal cheaply. The metal they obtained contained 96·5 per cent. of manganese, 2·0 of iron, and 1·5 of silicon.

A considerable amount of metallic manganese has been made by the Goldschmidt process (p. 737) of a high degree of purity. Lebeau[1] has, however, shown that metal so produced may contain as much as 5·25 per cent. of silicon.

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[1] *Ann. Chim. Phys.*, 1856, [3], **46**, 182.
[2] *Compt. rend.*, 1878, **86**, 1374.
[3] Brunner, *Pogg. Ann.*, 1857, **101**, 264.
[4] Glatzel, *Ber.*, 1889, **22**, 2857
[5] *Pogg. Ann.*, 1854, **91**, 619.
[6] Prelinger, *Monatsh.*, 1894, **14**, 353.
[7] *Trans. American Institute of Mining Engineers*, 1893, **21**, 887.

With regard to the preparation of manganese in the electric furnace,[2] Moissan proved that by using excess of oxide, the reduced metal might be obtained free from carbon and silicon. This method has recently been put into commercial use, but the efficiency of the process is not such as to yield metal at a low cost, for Moissan has shown that manganese is highly volatile at electric furnace temperatures, and that as much as 400 grams of the metal may be volatilised in ten minutes in the electric arc. High grade ferro-manganese, and other alloys such as silico-manganese, are produced in large quantities in electric furnaces.

Manganese has been obtained also by electrolysis. Ferro-manganese anodes are allowed to dip into fused sodium chloride, and an electric current is passed. Pure manganese is deposited at the cathode.[3] It has been prepared also by electrolysing manganese dioxide dissolved in fused fluorspar.[4]

Properties.—Small amounts of impurities influence the properties of manganese considerably; since none of the methods of preparing the metal yield an absolutely pure product, its properties depend largely on how it has been prepared. Obtained by the reduction process, it is a grey or reddish-white metal, having the colour and appearance of cast iron. It is very hard and brittle, has a specific gravity of about 7·3, and oxidises so easily in the air that it must be kept under rock-oil or in well-sealed vessels. Ferro-manganese is, however, unalterable in the air. Manganese is readily dissolved by all dilute acids, yields sulphur dioxide with hot concentrated sulphuric acid,[5] and decomposes water with evolution of hydrogen, even in the cold, more rapidly when heated. It melts[6] at 1260° and boils under atmospheric pressure at about 1900° (Greenwood)[7]; its atomic heat increases from 4·51 between the temperatures −188° and −79°, to 5·90 at 0°; 6·29 at 100°, and 9·09 at 500° (Estreicher and Staniewski[8]; Lammel[9]): its average compressibility between 100 and 500 megabars is 0·000,000,67 (Richards and Stull).[1] It is paramagnetic, but becomes ferromagnetic on heating: it is exceptional in that its magnetic properties are not intensified by cooling in solid hydrogen (Weiss and Kamerlingh Onnes).[2] Manganese combines rapidly with nitrogen above 1210°.

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[1] *Ann. Chim. Phys.*, 1904, 1, 553.

[2] *Compt. rend.*, 1892, **115**, 1429.

[3] Ger. Pat. 74959.

[4] Eng. Pat. 17190.

[5] Adie, *Proc. Chem. Soc.*, 1899, **15**, 133.

[6] Burgess and Waltenberg, *J. Washington Acad. Sci.*, 1913, **3**, 371.

[7] *Proc. Roy. Soc.*, 1909, **82**, [*A*], 396.

[8] *Bull. intern. Acad. Sci. Cracovie*, 1912, [*A*], 834.

[9] *Ann. Physik.*, 1905, (iv), **16**, 551.

515 *Alloys of Manganese.*—The alloys of manganese and copper closely resemble those of tin and copper.[3] Those which contain from 5 to 8 per cent. of manganese are malleable, but those in which a higher percentage of manganese is present become grey and brittle.

Manganese bronze is made by adding cupro-manganese containing about 25 per cent. of manganese to molten brass. For industrial purposes it contains from traces to 2 per cent. of manganese, 39 to 41 per cent. of zinc, and less than 1 per cent. each of tin, iron and aluminium, the rest being copper.

Manganin is a copper-manganese alloy containing small quantities of nickel. Its electrical resistance has a very low temperature coefficient, and it is largely used in the manufacture of electrical resistances.

Alloys of manganese with aluminium, antimony, tin, bismuth, arsenic, and boron are noteworthy owing to the remarkable magnetic properties which they possess.[4]

The alloys of manganese and iron, such as manganese steels, spiegel iron, and ferro-manganese, will be described under iron.

Manganese Amalgam is prepared by electrolysing a saturated solution of manganous chloride, mercury being used as the negative pole.

COMPOUNDS OF MANGANESE.

MANGANESE AND OXYGEN.

516 Manganese forms a series of oxides, of which the following are the best defined:

Manganese monoxide, MnO,
Trimanganese tetroxide, Mn_3O_4,
Manganese sesquioxide, Mn_2O_3,
Manganese dioxide, MnO_2,
Manganese trioxide, MnO_3,
Manganese heptoxide, Mn_2O_7.

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[1] *Pub. Carn. Inst.*, 1907, **76**, 55.

[2] *Compt. rend.*, 1910, **150**, 687.

[3] Valenciennes, *Compt. rend.*, 1870, **70**, 607.

[4] Hogg, *Brit. Assoc. Reports*, 1892, 671; Heusler, *Ber. deut. physikal. Ges.*, 1903, **5**, 220.

The first of these is a powerful basic oxide, whilst the sesquioxide is feebly basic, giving rise to an unstable series of salts, and the oxide, Mn_3O_4, behaves in many respects as a compound of the two. The dioxide acts as a weak acidic oxide, yielding with strong bases salts known as the manganites. Manganese trioxide and the heptoxide are well-marked acid-forming oxides. The manganates, derived from manganic acid, H_2MnO_4, are very unstable, and as already mentioned are isomorphous with the sulphates and chromates. Permanganic acid, $HMnO_4$, is a strong acid and yields stable salts, which are isomorphous with the perchlorates.

Manganese Monoxide, or *Manganous Oxide*, MnO, is best prepared by fusing together a mixture of equal parts of anhydrous manganese chloride and sodium carbonate to which some ammonium chloride has been added, and lixiviating the fused mass with water.[1] It is obtained also when a higher oxide or the carbonate is ignited in a current of hydrogen. Manganous oxide is a greyish-green powder, which fuses at 1650°[2] without loss of oxygen. It has a specific gravity of 5·09. When the powdered oxide is heated in hydrogen containing a very small quantity of hydrogen chloride, it is obtained crystallised in transparent, regular octahedra of an emerald-green colour and an adamantine lustre.[3] It has been found in Sweden as the crystalline mineral manganosite.

Manganous Hydroxide, $Mn(OH)_2$, is obtained as a white precipitate when caustic alkali is added to the solution of a manganese salt. As it oxidises rapidly in the air and assumes a brown colour, forming the oxide Mn_3O_4 and finally Mn_2O_3, it must be precipitated in an atmosphere free from oxygen, and dried at a moderate heat in a current of hydrogen. The powder thus obtained is frequently pyrophoric and when touched with a piece of red-hot charcoal it begins to glow at the point of contact, the oxidation proceeding rapidly throughout the mass. It occurs in Sweden as the mineral pyrochroite.

When ammonia is added to a solution of a manganous salt containing an ammonium salt, no immediate precipitation occurs, but on standing a precipitate separates out which consists of manganous hydroxide, if air be excluded, but of a brown hydrated oxide in the presence of air. When manganous hydroxide is treated with an ammonium salt it dissolves to an extent proportional to the concentration of ammonium ions in the solution; probably complex ions containing ammonium and manganese are formed.[1]

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[1] Liebig and Wöhler, *Pogg. Ann.*, 1830, **21**, 584.

[2] Tiede and Birnbrauer, *Zeit. anorg. Chem.*, 1914, **87**, 129.

[3] Deville, *Compt. rend.*, 1861, **53**, 199.

The manganous salts, MnR^I_2, are usually faintly pink-coloured, although, according to some chemists, this coloration is due to the presence of a trace of a manganic compound. The halogen salts, as well as the nitrate and sulphate, are readily soluble in water.

Mangano-Manganic Oxide, Red Oxide of Manganese, or *Trimanganese Tetroxide,* Mn_3O_4, occurs with other manganese ores, and also by itself as the mineral hausmannite. This mineral crystallises in acute tetragonal pyramids, and one of its best localities is Ilmenau in Thuringia. Its specific gravity is 4·85. If manganese monoxide is heated in contact with air, or if the higher oxides are strongly heated either in contact or out of contact with air, this same compound is obtained in the form of a brownish-red powder, which then has a specific gravity of 4·72, and is converted into crystals of hausmannite by being gently heated in a slow current of hydrogen chloride.[2] It is obtained in the crystalline form also by heating a mixture of manganese sulphate and potassium sulphate to bright redness,[3] or by treating a mixture of manganous oxide and calcium chloride in the same way.[4] This oxide dissolves in cold concentrated sulphuric acid, giving rise to a red solution containing a mixture of manganous and manganic sulphates, whilst acetic acid dissolves one-third of the manganese as manganous acetate and leaves the remainder in the form of the sesquioxide. Mixed oxides of the type Mn_2O_3,RO, which appear to be isomorphous with hausmannite (Gorgeu [5]), have been prepared by fusing the corresponding sulphates and by the ignition of the metallic manganites. Hence the red oxide is often considered to be a compound having the formula MnO,Mn_2O_3. On the other hand, other reactions suggest that it has the formula $2MnO,MnO_2$; thus, on heating with dilute sulphuric acid, manganous sulphate and manganese dioxide are formed, and boiling nitric acid decomposes it in a manner similar to that in which it acts on red lead:

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

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[1] Herz, *Zeit. anorg. Chem.*, 1899, **21**, 243; **22**, 279.

[2] Deville, *Compt. rend.*, 1861, **53**, 199.

[3] Debray, *Compt. rend.*, 1861, **52**, 985.

[4] Kuhlmann, *Compt. rend.*, 1861, **52**, 1283.

[5] *Bull. Soc. chim.*, 1903, [3], **29**, 1111, 1167.

Chlorine gas is given off when this oxide is heated with hydrochloric acid, and manganous chloride is formed:

$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2.$$

Manganic Oxide or *Manganese Sesquioxide*, Mn_2O_3.—This oxide occurs as the mineral braunite in obtuse tetragonal pyramids. It possesses a sub-metallic lustre, has a dark brownish-black colour, and a specific gravity of 4·75. It may be obtained artificially by igniting any of the oxides of manganese in a mixture of oxygen and nitrogen containing not more than twenty-six per cent. of oxygen.[1] It then forms a black powder, having a specific gravity of 4·32.

Manganic Hydroxide, MnO(OH), occurs in nature as manganite in steel-grey or arsenic-black crystals belonging to the tetragonal system, and having a specific gravity of 4·3. It is usually accompanied by other manganese ores, calc-spar, and heavy-spar. In general appearance it closely resembles pyrolusite but it may be distinguished from this compound by its giving a brown instead of a black streak when rubbed on an unglazed porcelain plate. When the mineral is heated at 270–310° in the air it is converted without change of form into the dioxide.[2] Manganic hydroxide is formed when manganous hydroxide is allowed to oxidise in moist air. It may be prepared also by passing chlorine into water in which an excess of manganese carbonate is suspended, or by decomposing the corresponding manganic sulphate with water (Carius).[3] It forms a dark-brown powder which gives off its water at a temperature above 100°. It dissolves in hot nitric acid:

$$2MnO(OH) + 2HNO_3 = Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

From this reaction it would appear that in constitution this body resembles lead sesquioxide and analogous compounds, having the constitution MnO,MnO_2, but in other reactions it acts as a feebly basic oxide, the salts of which, with a few exceptions, are very unstable.

The manganic salts, MnR_3 or $Mn_2R^{II}_3$, are unstable, strongly coloured substances. The fluoride, sulphate, phosphates, and salts of some organic acids are comparatively stable, as also are some double or complex salts, such as the double fluorides and chlorides, the manganicyanides, and the alums. Manganic chloride, bromide, iodate, periodate, selenite, and arsenate have been prepared.

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[1] Dittmar, *Journ. Chem. Soc.*, 1864, **17**, 204.

[2] Gorgeu, *Compt. rend.*, 1888, **106**, 1101.

[3] *Annalen*, 1856, **98**, 53.

MANGANESE DIOXIDE AND THE MANGANITES.

517 *Manganese Dioxide, Manganese Peroxide,* or *Black Oxide of Manganese*, MnO_2, is the most important ore of manganese. It occurs in rhombic crystals and in crystalline and amorphous masses, being known to the mineralogist as pyrolusite. It possesses a metallic lustre, an iron-black or dark steel-grey colour, and a black streak. It is opaque and rather brittle, and has a specific gravity of 4·82. The most celebrated localities for this mineral are Ilmenau in Thuringia, near Platten in Bohemia, near Mährisch-Trubau in Moravia, on the Lahn, and in the Caucasus, France, Spain, and North America. It occurs in the United States, abundantly at Vermont, and in Red Island Bay at San Francisco; and also in New Brunswick and Nova Scotia; large quantities too are found in India. It is likewise found in Devonshire. Pyrolusite seldom occurs in the pure state, but mixed with other manganese ores such as psilomelane, $(Mn,Ba)O,2MnO_2$, and manganite. It almost always contains ferric oxide, silica, lime, carbonic acid, and traces of the oxides of cobalt and nickel. Pure manganese dioxide is obtained by melting about 600 grams of the crystallised nitrate and warming until red fumes appear; the clear liquid is then decanted from the lower oxides which first separate out, and is heated in another vessel at 150–160° for 40–60 hours.[1] If manganous carbonate is heated to 260° in presence of air, and the residue then treated with very dilute cold hydrochloric acid, pure manganese dioxide remains behind (Forchhammer).

A brown precipitate approximating in composition to hydrated manganese dioxide can be obtained from the manganous salts by the aid of a large number of oxidising agents such as potassium permanganate (p. 1189), sodium hypochlorite, ammonia and bromine, nitric acid and sodium chlorate, ammonium persulphate and sulphuric acid,[2] and ozone.[3]

It appears to be almost impossible to prepare perfectly pure hydrated manganese peroxide,[4] since this substance very readily loses a portion of its oxygen, forming mixtures of the composition $x\mathrm{MnO} + y\mathrm{MnO_2}$, and moreover readily combines with bases forming manganites. Products of constant composition appear to be obtainable only from solutions acidified with a mineral acid.[1] Thus the oxide formed by the reduction of permanganic acid by manganese sulphate, and by the decomposition of permanganic acid in presence of hydrated manganese dioxide, varies in composition from $5MnO_2 + MnO$ to $15MnO_2 + MnO$. On the other hand, the oxide precipitated from manganous sulphate by dilute potassium permanganate at 80° in presence of zinc sulphate contains all the manganese in the form of dioxide, but combined with alkali. The oxide precipitated from manganese nitrate by nitric acid and sodium chlorate contains 98 per cent. of the manganese as dioxide,[2] and that obtained with ammonium persulphate also contains less than the theoretical amount of oxygen.[3] A similar oxide may also be prepared by treating manganic hydroxide with hot nitric acid,[4] or by adding potassium permanganate to sodium thiosulphate solution. The hydroxide thus obtained, after washing with water, is soluble in water, yielding a brown solution to which the name of manganous acid has been given. This solution turns blue litmus paper red, and does not undergo alteration on standing for many weeks, but small quantities of acid or alkali produce an instant precipitation. Manganous acid appears to be identical with a colloidal solution of manganese dioxide, which can be conveniently prepared by the action of ammonia on a boiling solution of potassium permanganate.[5] Manganese dioxide, like lead dioxide, possesses at the same time feebly basic and feebly acid properties. Of the salts in which manganese behaves as a quadrivalent basic element, only the chloride, sulphate, and selenite have been isolated. Among the most stable are certain double or complex salts, K_2MnF_6, K_2MnCl_6, $K_2Mn(IO_3)_6$.

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[1] Gorgeu, *Bull. Soc. chim.*, 1890, [3], **4**, 16.

[2] Marshall, *Journ. Chem. Soc.*, 1891, **59**, 771.

[3] Jannasch and Gottschalk, *Ber.*, 1904, **37**, 3111.

[4] Gorgeu, *Compt. rend.*, 1890, **110**, 1134.

On heating, manganese dioxide loses oxygen and forms the sesquioxide:

$$4MnO_2 = 2Mn_2O_3 + O_2.$$

The action is reversible; when the pressure of oxygen is below a certain value depending on the temperature the reaction goes towards the right hand side of the equation, when it is above that

[1] Rupp, *Zeit. anal. Chem.*, 1903, **42**, 732.

[2] Gooch and Austin, *Amer. J. Sci.*, 1898, [4], **5**, 260.

[3] von Knorre, *Zeit. angew. Chem.*, 1901, **14**, 1149.

[4] Gorgeu, *Ann. Chim. Phys.*, 1862, [3], **66**, 155.

[5] Guy, *J. Physical Chem.*, 1921, **25**, 415.

value towards the left.[1] When heated to higher temperatures the red oxide, Mn_3O_4, is produced.

Manganese dioxide has long been used for the preparation of colourless glass, and hence pyrolusite has been known as *savon des verriers*. Its mineralogical name, indeed, has reference to this employment of the mineral (from πῦρ, fire, and λύω, *I* wash). It serves also for the preparation of the manganese compounds and of oxygen, but by far the largest quantity of the mineral is employed for making chlorine, used in the manufacture of bleaching powder.

The Manganites.—Manganese dioxide combines with several basic oxides to form compounds which may be considered as salts of manganous acid. The composition of these compounds seems to depend on the amount of alkali which is present. A large number of them have been described. *Potassium Manganite*, $K_2Mn_5O_{11}$, is obtained as a yellow precipitate when carbon dioxide is passed into a solution of potassium manganate, K_2MnO_4. *Calcium Manganite*, $CaMn_5O_{11}$, is a blackish-brown precipitate formed when a solution of manganous nitrate is poured into an excess of bleaching powder solution. Many other compounds, such as Ca_2MnO_4, $CaMnO_3$, $CaMn_2O_5$, and $CaMn_3O_7$, have been prepared.

518 *Regeneration of Manganese Dioxide from the Chlorine Residues.*—Before the year 1856 the whole of the manganese chloride obtained in the manufacture of chlorine from manganese dioxide and hydrochloric acid was allowed to run to waste. In 1821 Forchhammer[2] observed that when manganous carbonate is heated to 260° in an open vessel it is converted into dioxide. Charles Dunlop[3] applied this reaction to the regeneration of manganese dioxide from the chlorine still liquors, the manganous carbonate being prepared by heating manganous chloride solution with calcium carbonate under pressure. In 1857 this process was adopted by Messrs. Charles Tennant and Co., at St. Rollox, but the process was not adopted elsewhere.

A much less troublesome process was invented by Walter Weldon, in 1867, and first practically carried out at Messrs. Gamble's works at St. Helens in 1868; it is now universally adopted wherever chlorine is made from manganese dioxide and hydrochloric acid.

The crude manganese chloride solution remaining in the stills,

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[1] Askenasy and Klonowski, *Zeit. Elektrochem.*, 1910, **16**, 107.

[2] *Ann. Phil.*, 1821, **17**, 50.

[3] *Report of Patent Inventions*, March, 1856, p. 236.

I (Fig. 190), which are fitted for using native manganese dioxide, is run into the well, K, and treated with limestone dust, which neutralises the residual free hydrochloric acid, precipitates the sulphuric acid present as impurity in the hydrochloric acid in the form of calcium sulphate, and then precipitates the ferric chloride as ferric hydroxide; the muddy liquor is thrown by the pump, L, into the settling tanks, A, from which the clear manganous chloride solution is run into the oxidiser, B, while the sediment is run into the shute, H, and so to the drains. In the agitator, E, lime is slaked to form a thick cream which is run through a sieve into a store and measuring tank, whence it is pumped as required into the oxidiser, B.

If exactly the theoretical amount of milk of lime be added according to the equation:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2,$$

it is found that the whole of the manganese is not precipitated and the mixture absorbs oxygen exceedingly slowly, only half the manganese being converted into dioxide; by adding ten per cent. more lime the liquor becomes free from manganese, but the most rapid absorption of oxygen and the most readily settling mud are obtained only by employing about sixty per cent. more lime (Weldon). When air is pumped by the pipe, C, through this mixture at 55°, the alkalinity disappears owing, to the formation of calcium manganite, CaO,MnO_2, and acid manganite, $CaO,2MnO_2$, whilst some of the manganous oxide is converted into manganous manganite, MnO,MnO_2:

$$100MnO + 60CaO + 86O = 12(CaO,2MnO_2) + 48(CaO,MnO_2) + 14(MnO,MnO_2),$$

at about which stage the oxidation practically ceases. An additional quantity of the manganous chloride is next added, which instantly reacts with the CaO,MnO_2, thus:

$$48(CaO,MnO_2) + 24MnCl_2 = 24(CaO,2MnO_2) + 24MnO + 24CaCl_2,$$

and the blowing being continued, the manganous oxide is oxidised to manganous manganite:

$$24MnO + 12O = 12(MnO,MnO_2).$$

The effect of the whole operation may be summarised thus:

$$124MnCl_2 + 160CaO + 98O = 36(CaO,2MnO_2) + 26(MnO,MnO_2) + 124CaCl_2.$$

value towards the left.[1] When heated to higher temperatures the red oxide, Mn_3O_4, is produced.

Manganese dioxide has long been used for the preparation of colourless glass, and hence pyrolusite has been known as *savon des verriers*. Its mineralogical name, indeed, has reference to this employment of the mineral (from πῦρ, fire, and λύω, *I* wash). It serves also for the preparation of the manganese compounds and of oxygen, but by far the largest quantity of the mineral is employed for making chlorine, used in the manufacture of bleaching powder.

The Manganites.—Manganese dioxide combines with several basic oxides to form compounds which may be considered as salts of manganous acid. The composition of these compounds seems to depend on the amount of alkali which is present. A large number of them have been described. *Potassium Manganite*, $K_2Mn_5O_{11}$, is obtained as a yellow precipitate when carbon dioxide is passed into a solution of potassium manganate, K_2MnO_4. *Calcium Manganite*, $CaMn_5O_{11}$, is a blackish-brown precipitate formed when a solution of manganous nitrate is poured into an excess of bleaching powder solution. Many other compounds, such as Ca_2MnO_4, $CaMnO_3$, $CaMn_2O_5$, and $CaMn_3O_7$, have been prepared.

518 *Regeneration of Manganese Dioxide from the Chlorine Residues.*—Before the year 1856 the whole of the manganese chloride obtained in the manufacture of chlorine from manganese dioxide and hydrochloric acid was allowed to run to waste. In 1821 Forchhammer[2] observed that when manganous carbonate is heated to 260° in an open vessel it is converted into dioxide. Charles Dunlop[3] applied this reaction to the regeneration of manganese dioxide from the chlorine still liquors, the manganous carbonate being prepared by heating manganous chloride solution with calcium carbonate under pressure. In 1857 this process was adopted by Messrs. Charles Tennant and Co., at St. Rollox, but the process was not adopted elsewhere.

A much less troublesome process was invented by Walter Weldon, in 1867, and first practically carried out at Messrs. Gamble's works at St. Helens in 1868; it is now universally adopted wherever chlorine is made from manganese dioxide and hydrochloric acid.

The crude manganese chloride solution remaining in the stills, the chlorine made entirely from the mud, and as this, unlike the native ores, contains no iron which requires to be eliminated by precipitation with limestone dust, it now becomes possible to avoid the use of the latter and to utilise the excess of acid which is invariably left in the chlorine still, even when the artificial mud is used. But as crude hydrochloric acid always contains sulphuric acid, which was eliminated as calcium sulphate in the mud run off from the settling tanks, A, in the process so far described, it is necessary to provide a new outlet for this impurity, and this is done by treating the hydrochloric acid with a portion of the waste calcium chloride liquor, the calcium sulphate formed being separated by a sand-filter. The purified acid is then used to generate chlorine in the stone stills I, with thick manganese mud run from the settlers, G, by the pipe, N. When no more chlorine is evolved the residual liquor is treated with an excess of mud more than enough to neutralise all the residual free acid, amounting to about 0·7 per cent. of the liquor; the mixture is then allowed to settle, and the much richer manganese mud settling out forms part of the next batch to be treated with acid, the reaction being approximately:

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[1] Askenasy and Klonowski, *Zeit. Elektrochem.*, 1910, **16**, 107.

[2] *Ann. Phil.*, 1821, **17**, 50.

[3] *Report of Patent Inventions*, March, 1856, p. 236.

$$36(CaO,2MnO_2) + 18HCl = 18MnO_2 + 27(CaO,2MnO_2) + 9CaCl_2 + 9H_2O.$$

The Weldon operation thus converts $124MnCl_2$ into $98MnO_2 + 26MnO$. The equations given above are intended to express the average results obtained.[1]

MANGANESE TRIOXIDE AND HEPTOXIDE, MANGANIC ACID, PERMANGANIC ACID, AND THEIR SALTS.

519 In his work entitled *The Prosperity of Germany*,[2] published in 1656, Glauber mentions that when manganese is fused with fixed saltpetre (caustic potash) a mass is produced from which he obtained "a most dainty purple fiery liquor," this afterwards turning blue, red, and green. In 1705 an anonymous treatise appeared, entitled *Key to the Secret Cabinet of Nature's Treasury;* in this it is stated that the product obtained by fusing saltpetre and manganese yields a solution of which the colour alters, first being grass-green, then sky-blue, violet-coloured, and

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[1] A detailed description is to be found in Lunge's *Sulphuric Acid and Alkali Manufacture*, Vol. III.

[2] Packe's translation, 1687, p. 353.

lastly rose-red. The changes of colour which are here given are exactly the opposite of those which Glauber noticed. Pott in 1740 described these changes, believing that they had not been previously noticed, and Scheele, who endeavoured to explain these phenomena, gave to the colouring material the name of mineral chameleon, a term which had previously been applied to other mineral colouring matters capable of undergoing changes of tint. The properties of this mineral chameleon were afterwards investigated by many chemists, but it was not until the year 1817, when Chevillot and Edwards [1] investigated the subject, that a rational view of its composition was arrived at. They showed that when much alkali is employed a green compound is formed; that when, on the other hand, an excess of manganese is fused with potash a red body is produced, and they succeeded in preparing the substance obtained by the latter reaction in the crystalline form. They also showed that an absorption of oxygen takes place, and consequently they assumed that the potash salt forms with manganese a manganate, and that the green salt contains more base than the red. Forchhammer [2] investigated the subject in 1820, and ascribed the difference in colour to the existence of two distinct acids; but Mitscherlich [3] first showed their exact composition.

Manganese Trioxide, MnO_3, is a deliquescent, amorphous, reddish mass, prepared by dropping a solution of potassium permanganate in concentrated sulphuric acid on to dry sodium carbonate: [4]

$$2(MnO_3)_2SO_4 + 2Na_2CO_3 = 2Na_2SO_4 + 4MnO_3 + 2CO_2 + O_2.$$

It is formed only in extremely small quantity, and is carried forward by the carbon dioxide as a pink fume, which may be caught on fragments of glass placed in a freezing mixture.

When thrown into water it is decomposed as follows: [5]

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2.$$

The *manganates* have a green colour, and their solutions are stable only when they contain large quantities of free alkali. If carbon dioxide is passed through them, or if they are diluted with much water, or made slightly acid, the liquid passes from a green to a blue and violet colour, the permanganate being formed, and the dioxide deposited:

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[1] *Ann. Chim. Phys.*, 1817, [2], 4, 287.

[2] *Ann. Phil.*, 1820, 16, 130; 1821, 17, 150.

[3] *Pogg. Ann.*, 1832, 25, 287.

[4] Franke, *J. pr. Chem.*, 1887, [2], 6, 393.

[5] Thorpe and Hambly, *Journ. Chem. Soc.*, 1888, 53, 175.

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

The manganates are also converted by direct oxidation into permanganates when they are dissolved in a large quantity of water containing dissolved oxygen.

Manganates are produced by the partial reduction of permanganates in alkaline solution, and this change occurs when small amounts of reducing agents such as alcohol and sodium thiosulphate are added to the red, alkaline liquid. The latter also gradually turns blue and afterwards green simply on exposure to air, this being caused by the reducing action of the organic matter contained in the atmosphere. These reactions explain the changes of colour of the mineral chameleon. In alkaline solution the manganates act as powerful oxidising agents.

Potassium Manganate, K_2MnO_4.—The preparation of potassium manganate is important, since it is the first stage in the manufacture of potassium permanganate. Potassium hydrate or carbonate is heated with manganese dioxide to dull redness in the presence of air; in the laboratory it is quicker and therefore more convenient to use an oxidising agent such as potassium chlorate. According to Bahr and Sackur,[1] the product is a complex manganite-manganate:

$$8K_2CO_3 + 5MnO_2 + 3O = 8K_2O,Mn_5O_{13} + 8CO_2.$$

The deep green-coloured mass is dissolved in water, when manganese dioxide is precipitated and an alkaline solution of manganate is obtained:

$$8K_2O,Mn_5O_{13} + 5H_2O = 3K_2MnO_4 + 2MnO_2 + 10KOH.$$

By evaporation of the resulting deep green solution, after it has been separated from the precipitated dioxide by decantation and filtration, the salt is obtained in small crystals isomorphous with those of potassium sulphate. It may be prepared also by boiling a saturated solution of potassium permanganate with caustic potash solution of specific gravity 1·33 (Aschoff).

On heating it is decomposed, potassium manganite and oxygen being formed:

$$2K_2MnO_4 = 2K_2MnO_3 + O_2.$$

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[1] *Zeit. anorg. Chem.*, 1912, 73, 101. See also Askenasy and Klonowski, *Zeit. Elektrochem.*, 1910, 16, 104.

The reaction does not go to completion, however, for the manganite forms a solid solution or complex manganite-manganate with the unchanged manganate of the composition $5K_2O,Mn_5O_{13}$ or $3K_2MnO_4,2K_2MnO_3$; this does not decompose easily (Bahr and Sackur).

Sodium Manganate, Na_2MnO_4, is formed when a mixture of equal parts of manganese dioxide and caustic soda is heated for sixteen hours; the mass is then lixiviated with a small quantity of water and the solution cooled down, when the salt separates out in small crystals isomorphous with Glauber's salt, and having the composition $Na_2MnO_4,10H_2O$. These dissolve in water with partial decomposition, yielding a green solution. Sodium manganate is now used largely as a deodoriser.

Barium Manganate, $BaMnO_4$, is formed when manganese dioxide is heated with baryta or barium carbonate or nitrate, or when barium permanganate is heated with baryta-water. It is an emerald-green powder, consisting of microscopic, four-sided prisms or six-sided plates. It has a specific gravity of 4·85, and is insoluble in water, but is readily decomposed by acids. The employment of this salt in place of the poisonous Scheele's green has been suggested,[1] and it has been employed in a few instances, though not so generally as might be wished.

520 *Manganese Heptoxide*, Mn_2O_7, and *Permanganic Acid*, $HMnO_4$.—The first of these compounds, also termed permanganic anhydride, was noticed by Chevillot, and afterwards investigated by Thénard,[2] Aschoff,[3] and Terreil.[4] In order to prepare this compound, pure potassium permanganate free from chlorine is gradually added to well-cooled, highly concentrated sulphuric acid. The salt dissolves with an olive-green colour,

$$2KMnO_4 + 2H_2SO_4 = (MnO_3)_2SO_4 + K_2SO_4 + 2H_2O,$$

and if the solution be cooled, and water carefully added, the heptoxide separates as a dark reddish-brown liquid[5] which does not solidify at $-20°$:

$$(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4.$$

It is extremely unstable, constantly evolving bubbles of oxygen on exposure to the air. These carry with them a small quantity of the heptoxide, and thus violet fumes are emitted. It rapidly absorbs moisture, and dissolves in water, yielding a deep violet-coloured solution, so much heat being thereby evolved that the liquid undergoes partial decomposition. It dissolves in concentrated sulphuric acid with an olive-green colour. On heating, it decomposes, with evolution of light and heat, and with violent explosion.

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[1] Schad, *Deutsch. Industriezeit.*, 1865, 118; Rosenstiehl, *Dingl. Polyt. Journ.*, 1865, **177**, 409.

[2] *Compt. rend.*, 1856, **42**, 389.

[3] *Pogg. Ann.*, 1860, **111**, 217.

[4] *Bull. Soc. chim.*, 1862, 40.

[5] Franke, *J. pr. Chem.*, 1885, [2], **31**, 166.

Permanganic Acid, $HMnO_4$, is obtained in aqueous solution by adding the requisite quantity of dilute sulphuric acid to the barium salt or by electrolysing the potassium salt in a special form of apparatus and removing the alkali from the cathode compartment.[1] A deep red liquid is thus obtained, which exhibits a blue colour by reflected light, and possesses a bitter, metallic taste. It decomposes on exposure to light or when heated gently, and still more rapidly when boiled, with evolution of oxygen and separation of the hydrated dioxide. It acts as a most powerful oxidising agent.

Permanganic acid is formed also when manganese nitrate or any manganous salt, with the exception of the halide compounds, is warmed with nitric acid and lead dioxide, with potassium bromate and dilute sulphuric acid,[2] with the higher oxides of bismuth and nitric acid,[3] or with ammonium persulphate, silver nitrate, and nitric acid.[4]

A weak solution of permanganic acid continually evolves oxygen at a very slow rate, manganese dioxide being deposited, and the rate of decomposition is greatly increased by the presence of hydrated manganese dioxide.[5] When such a solution is shaken with hydrogen or carbonic oxide, the gas is rapidly absorbed and a considerable volume of oxygen evolved (Victor Meyer and Recklinghausen).[6] It has been suggested that this is due to the fact that the hydrated manganese dioxide simultaneously formed is at first present in a specially active condition and thus greatly increases the normal decomposition of the permanganic acid (Morse and Reese).

Permanganic acid has been obtained in the form of violet-black crystals by evaporating the solution obtained by the action of barium permanganate and sulphuric acid. It decomposes very rapidly.[1]

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[1] Morse and Olsen, *Amer. Chem. J.*, 1900, **23**, 431.

[2] Vitali, *Boll. Chim. Farm.*, 1898, **37**, 545.

[3] Schneider, *Dingl. Polyt. Journ.*, 1888, **269**, 224.

[4] Marshall, *Chem. News*, 1901, **83**, 76.

[5] Morse, Hopkins, and Walker, *Amer. Chem. J.*, 1896, **18**, 401; Morse, *Ber.*, 1897, **30**, 48; Morse and Reese, *Amer. Chem. J.*, 1898, **20**, 521; Morse and Byers, *ibid.*, 1900, **23**, 313; Olsen, *ibid.*, 1903, **29**, 242.

[6] *Ber.*, 1896, **29**, 2549; Hirtz and Meyer, *ibid.*, 2828.

Potassium Permanganate, $KMnO_4$, is prepared on the large scale as a disinfectant. The first stage is the preparation of an alkaline solution of potassium manganate (*q.v.*). This may be neutralised by carbon dioxide or sulphuric acid; manganates are only stable in presence of alkali, and when this is removed they decompose according to the equation :

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

This method involves the loss of two-thirds of the manganese and the neutralisation of the alkali. The loss of manganese is prevented by Stadeler's method of passing chlorine into the solution, but this method is just as wasteful of the alkali.

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl.$$

An electrolytic process of oxidation is now largely used. This involves no loss of manganese, nor is the alkali neutralised, and the resulting permanganate has only to be separated from the very soluble hydroxide. Numerous processes[2] have been described; in most the solution is electrolysed between iron electrodes separated by a diaphragm. Oxidation takes place at the anode, thus :

$$2K_2MnO_4 + H_2O + O = 2KMnO_4 + 2KOH.$$

When the pure crystallised product is not required, the corresponding, difficultly crystallisable, but cheaper, sodium permanganate is prepared in an exactly similar manner; solutions of this are sold as *Condy's Disinfecting Fluid.*

Potassium permanganate is isomorphous with potassium perchlorate, with which it crystallises in all proportions. The crystals are almost black, and when freshly prepared possess a green, metallic lustre, which, however, on exposure to the air becomes of a steel-blue tint without any further alteration in the salt taking place. The crystals have a specific gravity of 2·7, and yield a red powder. One hundred parts of water dissolve[3] 2·83 parts of the salt at 0°, 6·34 parts at 19·8°, 12·56 parts at 40°, and 25·03 parts at 65°, forming a deep purple-coloured solution. On heating to 240° they decompose as follows:

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[1] Muir, *Journ. Chem. Soc.*, 1907, **91**, 1485.

[2] See Brand and Ramsbottom, *J. pr. Chem.*, 1910, [2], **82**, 336; Askenasy and Klonowski, *Zeit. Elektrochem*, 1910, **16**, 170.

[3] Baxter, Boylston, and Hubbard, *J. Amer. Chem. Soc.*, 1906, **28**, 1336; Patterson, *ibid.*, 1734.

$$10KMnO_4 = 2K_2MnO_3 + (3K_2MnO_4 + 5MnO_2) + 6O_2.$$

The final products are potassium manganite and a solid solution or complex compound of potassium manganate with manganese dioxide.[1]

Jones[2] has shown that hydrogen and phosphine decompose potassium permanganate, and that oxygen is evolved together with carbon dioxide when sulphuric acid acts on permanganate in presence of oxalic acid.

Mixed with sulphur or phosphorus, a material is obtained which takes fire or explodes violently on percussion, and a mixture of the salt with charcoal burns like tinder.

Potassium permanganate is largely used as an oxidising agent, both in analytical work and for the preparation of many organic oxidation products. In alkaline solution it is first converted into manganate, which afterwards loses a further amount of oxygen and yields the hydrated dioxide, two molecules of the salt providing three atoms of oxygen.

$$(1)\ 2KMnO_4 + 2KHO = 2K_2MnO_4 + H_2O + O,$$
$$(2)\ 2K_2MnO_4 + 2H_2O = 2MnO_2 + 3KHO + 2O.$$

It is in this way, for example, that potassium permanganate acts when it is brought into contact with a hot solution of manganous salt, the whole of the manganese being precipitated as dioxide (Volhard); three-fifths of this is therefore formed by the oxidation of the manganese salt added and the remaining two-fifths by the reduction of the permanganate:

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

In acid solution the manganese of the permanganate is finally converted into a salt corresponding to the monoxide MnO, five atoms of oxygen being rendered available:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Thus the action of acid potassium permanganate solution on ferrous sulphate, in presence of sulphuric acid, is represented:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

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[1] Askenasy and Solberg *Nernst-Festschrift*, 1912, 53.

[2] *Journ. Chem., Soc.*, 1878, 33, 95.

The acid solution of potassium permanganate is reduced by hydrogen peroxide with evolution of oxygen,[1] half of which is due to the peroxide, half to the permanganate:

$$2KMnO_2 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

The reduction of potassium permanganate by formic acid in slightly acid solution appears to take place in stages.[2]

When potassium permanganate is used as an oxidising agent in volumetric analysis, it is often noticed that the first portion of permanganate added only reacts slowly, further additions react more rapidly. The phenomenon is particularly noticeable in the titration of oxalic acid. This is an example of *autocatalysis*: manganous sulphate catalyses, and is itself a product of the reaction. Harcourt and Esson,[3] and Schilow,[4] have shown that the velocity of the reaction is proportional to the concentration of the manganous salt. Similar results have been obtained in the oxidation of sulphites, and in the titration of hydrogen peroxide. In the titration of ferrous salts in the presence of hydrochloric acid, besides the main reaction shown in the equation above, a subsidiary reaction, induced by the presence of iron salts, occurs:

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

This secondary reaction can be prevented by the addition of manganous sulphate, which greatly increases the velocity of the main, but not that of the secondary reaction; thus a negligible part of the permanganate only is used in the oxidation of the hydrochloric acid.

Ammonium Permanganate, NH_4MnO_4, is obtained by the decomposition of the potassium salt with ammonium chloride. It is isomorphous with potassium permanganate, and decomposes readily when gently heated,[5] forming ammonium nitrate, oxides of nitrogen, and an oxide of manganese of the composition $22MnO_2,MnO$. It explodes when rapidly heated, or when subjected to percussion.

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[1] On the nature of this reaction, see Baeyer and Villiger, *Ber.*, 1900, 33, 2488, where the literature is quoted; Bach, *Ber.*, 1901, 34, 3851.

[2] Holluta, *Zeit. physikal Chem.*, 1922, 101, 34.

[3] *Phil. Trans.*, 1866, 156, 201.

[4] *Ber.*, 1903, 36, 2735.

[5] Christensen, *Zeit. anorg. Chem.*, 1900, 24, 203.

Barium Permanganate, $Ba(MnO_4)_2$, forms hard, almost black prisms, soluble in water. It is obtained by passing carbon dioxide through water containing barium manganate in suspension,[1] or by the action of barium chloride on silver permanganate.

Silver Permanganate, $AgMnO_4$, separates out in large, regular crystals when warm solutions of silver nitrate and potassium permanganate are mixed. It dissolves in 190 parts of water at 15°, and is much more soluble in warm water. The solution decomposes on boiling.

MANGANESE AND THE HALOGENS.

521 *Manganous Fluoride*, MnF_2, is obtained by dissolving metallic manganese or the carbonate in hydrofluoric acid, the compound being deposited as a white, crystalline powder when the solution is boiled. According to Edminster and Cooper,[2] however, the compound thus formed is an acid salt, $MnF_2,5HF,6H_2O$, of specific gravity 1·921. It is formed as a rose-coloured mass by the action of gaseous hydrogen fluoride on manganese. It is insoluble in water, but may be recrystallised from fused manganese chloride and then forms rose-coloured prisms of sp. gr. 3·98, melting at 856°. It dissolves in strong acids, yields an oxyfluoride when boiled with water, and is completely reduced by hydrogen at 1000°.[3]

Manganic Fluoride, MnF_3, is obtained by the action of fluorine on manganous iodide in purple pseudomorphs of sp. gr. 3·54. It decomposes, when heated, into manganous fluoride and fluorine, dissolves in strong acids, forming unstable dark brown solutions, and is decomposed by water.[4] A hydrated trifluoride, $MnF_3,3H_2O$, is obtained in ruby-red crystals by dissolving the sesqui- or the di-oxide in hydrofluoric acid.

Potassium Manganifluoride, K_2MnF_6, is obtained by decomposing potassium manganate with water and dissolving the resulting potassium manganite in a mixture of hydrofluoric acid and potassium fluoride. It forms small, golden-yellow, hexagonal tablets and is decomposed by water, but may be recrystallised from hydrofluoric acid. It yields a dark brown-coloured solution in hydrochloric acid which evolves chlorine when gently heated. A *rubidium salt* of similar properties has also been obtained.[1]

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[1] Böttger, *J. pr. Chem.*, 1863, **90**, 156.

[2] *J. Amer. Chem. Soc.*, 1920, **42**, 2419.

[3] Moissan and Venturi, *Compt. rend.*, 1900, **130**, 1159.

[4] Moissan, *Compt. rend.*, 1900, **130**, 622.

Manganous Chloride, $MnCl_2$, is formed when the metal is burned in chlorine gas, or when hydrogen chloride is passed over heated manganous carbonate. Prepared in this way, manganese chloride is a pale rose-coloured mass, having a lamino-crystalline structure. When heated to redness it fuses to an oily liquid, and decomposes in moist air at this temperature with formation of hydrochloric acid and the oxides of manganese. Manganous chloride is obtained in solution by dissolving the carbonate or any of the oxides in hydrochloric acid. For this purpose the residues from the preparation of chlorine by means of pyrolusite and hydrochloric acid may be utilised. These are always coloured yellow, from the presence of ferric chloride, and contain an excess of acid. They must be evaporated to drive off the acid, then diluted with water, and a tenth of the solution precipitated with sodium carbonate. The precipitate, consisting of manganese carbonate and ferric hydroxide, is then well washed with hot water and boiled with the remainder of the liquid for a long time. By this means the whole of the iron is precipitated as ferric oxide. The filtrate may contain copper, barium, and calcium, which are separated by the usual methods. On evaporation, a concentrated solution of manganous chloride deposits between 15° and 20° light pink-coloured, monoclinic crystals of the hydrate $MnCl_2,4H_2O$. This hydrate is transformed at 58·098° into the hydrate $MnCl_2,2H_2O$, this temperature having been determined with great accuracy by Richards and Wrede as a suitable fixed point for use in thermometry.[2] The dihydrate is stable up to 198° and then passes into the anhydrous salt. Below − 2° the hydrate $MnCl_2,6H_2O$ is formed.[3] In addition to these an isomeric β-tetrahydrate is known (Marignac)[4] which also forms monoclinic crystals, but of a different form from the ordinary tetrahydrate, being isomorphous with those of hydrated ferrous chloride, $FeCl_2,4H_2O$. The dihydrate may be prepared by heating the tetrahydrate for some time at 60° or passing hydrogen chloride into an alcoholic solution of the chloride. One hundred parts of water dissolve:

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[1] Weinland and Lauenstein, *Zeit. anorg. Chem.*, 1899, **20**, 40.

[2] *Zeit. physikal. Chem.*, 1907, **61**, 313.

[3] Kuznetzoff, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 741; Dawson and Williams, *Zeit. physikal. Chem.*, 1899, **31**, 59. See also Richards and Briggs, *ibid.*, 1898, **28**, 313.

[4] *Compt. rend.*, 1857, **45**, 650.

At	8°	25°	30°	57·85°	80°	100°.
$MnCl_2$	62	77·2	80·7	105·7	112·7	116.

This salt is also soluble in alcohol, forming a green solution which burns on ignition with a red flame. Manganous chloride forms double salts with the chlorides of the alkali metals, such as $K_2MnCl_4,2H_2O$ and K_4MnCl_6, and with the chlorides of some other metals. The anhydrous salt combines readily with ammonia and similar compounds. With ammonia, it forms the hexammine, $[Mn(NH_3)_6]Cl_2$, the diammine, $(NH_3)_2,MnCl_2$, and the monammine, $NH_3,MnCl_2$.[1]

Manganese Trichloride, $MnCl_3$, and *Manganese Tetrachloride*, $MnCl_4$, have only recently been obtained in the solid state. When any one of the oxides, Mn_3O_4, Mn_2O_3, or MnO_2, is added to cold concentrated hydrochloric acid, a dark brown solution is formed, chlorine being simultaneously produced when the dioxide is employed. This solution appears to contain the trichloride,[2] and yields double salts of the type $MnCl_3,2RCl$, with the chlorides of potassium and ammonium.[3] The addition of water to the solution precipitates a mixture of hydrated oxides (Pickering).[4] When the dark brown solution is heated, chlorine is evolved,

$$2MnCl_3 = 2MnCl_2 + Cl_2.$$

When manganese dioxide is treated with ether saturated with hydrochloric acid, a deep green solution is obtained, which was considered by Nicklés [5] to contain the tetrachloride, $MnCl_4$, and by Franke [6] to contain the compound $MnCl_2,MnCl_4$. It is, however, probable that this green liquid contains the trichloride and not the tetrachloride, since it yields double salts with the hydrochlorides of pyridine and quinoline of the type $MnCl_3,2RHCl$; almost the whole of the manganese in the solution can be precipitated in this form. More concentrated green solutions can be prepared by the action of alcoholic hydrochloric acid on manganese dioxide or potassium permanganate.[1]

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[1] Biltz and Huttig, *Zeit. anorg. Chem.*, 1919, **109**, 88; Ephraim, *Ber.*, 1912, **45**, 1322; *Zeit. physikal. Chem.*, 1913, **81**, 513.

[2] Pickering, *Journ. Chem. Soc.*, 1879, **35**, 654.

[3] Neumann, *Monatsh.*, 1894, **15**, 489; Rice, *Journ. Chem. Soc.*, 1898, **73**, 258.

[4] See also Fisher, *Journ. Chem. Soc.*, 1878, **33**, 409; Christensen, *J. pr. Chem.*, 1887, [2], **35**, 57, 161, 541.

[5] *Ann. Chim. Phys.*, 1865, [4], **5**, 169; 1867, [4], **10**, 318.

[6] *J. pr. Chem.*, 1888, [2], **36**, 31, 453.

When dry hydrogen chloride is passed into carbon tetrachloride in which manganese dioxide is suspended, a solid product is obtained which consists of manganese trichloride and tetrachloride. On treating this with anhydrous ether, the trichloride dissolves, forming a deep violet-coloured solution. A reddish-brown residue of the tetrachloride remains. The trichloride is a black solid, having a greenish tinge, which is decomposed by water. The tetrachloride is stable at ordinary temperatures, but is decomposed by moisture.[2]

Derivatives of the tetrachloride can be obtained by boiling potassium permanganate with glacial acetic acid, and saturating the resulting reddish-brown solution with hydrochloric acid. A dark crystalline precipitate of *potassium manganichloride*, $MnCl_4,2KCl$, is thus produced, which rapidly loses chlorine in moist air, but may be preserved in dry air for some time. If potassium acetate be added to the liquid before it is saturated with hydrochloric acid, Neumann's salt, $MnCl_3,2KCl$, is obtained (Meyer and Best).

Permanganic Oxychloride, MnO_3Cl.—This chloride of permanganic acid was first prepared by Dumas;[3] he did not, however, analyse the compound, but from its mode of decomposition considered it to be manganese heptachloride, $MnCl_7$. It is obtained by gradually adding fused sodium chloride to a solution of potassium permanganate in concentrated sulphuric acid. A yellow gas is then evolved, which when passed through a freezing mixture condenses to a greenish-brown liquid. This when exposed to the air emits a purple-red vapour, which possesses the peculiar smell of the oxides of chlorine, and like them acts most violently upon the mucous membrane, so that the smallest quantity of the chloride contained in commercial permanganate can be thus readily detected.[4] When heated, it explodes violently, and water decomposes it with formation of permanganic acid and hydrochloric acid. These substances, however, mutually decompose with formation of free chlorine and manganese dioxide. A corresponding oxyfluoride, MnO_3F, exists, and was first prepared by Wöhler.[5]

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[1] Meyer and Best, *Zeit. anorg. Chem.*, 1900, **22**, 169.

[2] Holmes, *J. Amer. Chem. Soc.*, 1907, **29**, 1277.

[3] *Ann. Chim. Phys.*, 1827, [2], **36**, 81.

[4] Aschoff, *Pogg. Ann.*, 1860, **111**, 217.

[5] *Pogg. Ann.*, 1827, **9**, 619.

Manganous Bromide, $MnBr_2$, is obtained by heating the powdered metal in bromine vapour, and when the compound is fused, it is obtained as a pale red mass. It can also be obtained by the action of the calculated quantity of bromine on finely divided manganese suspended in ether, but not in other organic solvents. The crystalline compound $MnBr_2,(C_2H_5)_2O$ is first obtained; this readily loses its ether on being heated to 100°, leaving manganous bromide as a white powder (Ducelliez and Raynaud).[1] When the carbonate is dissolved in hydrobromic acid the hydrated bromide, $MnBr_2,4H_2O$, is obtained, and this was found by Marignac to be isomorphous with the ordinary form of the chloride. Other hydrates are known. Unlike the chloride, it shows no tendency to form double salts with chlorides of the alkali metals. It behaves in a similar manner to the chloride towards ammonia (Biltz, Ephraim).

Manganic Bromide, $MnBr_3$.—When finely divided manganese is treated with a large excess of bromine in ethereal solution, two liquid layers are formed; from the lower of these Ducelliez and Raynaud obtained by cautious evaporation a yellow, amorphous mass of the composition $MnBr_3,3(C_2H_5)_2O$, from which the ether could not be removed without formation of manganous bromide. It is very soluble in water, and gives a black precipitate with sodium carbonate solution.

Manganous Iodide, $MnI_2,4H_2O$, is obtained crystallised in colourless, deliquescent needles, which become coloured on exposure to air. Hydrates with $6H_2O$ and $9H_2O$ are formed below − 2·7° and − 9·3° respectively.[2] It has little tendency to form double salts, and forms a hexammine and a diammine (Biltz, Ephraim).

Manganese Tetriodate, $Mn(IO_3)_4$, is not known in the free state, but a double salt with potassium iodate, $Mn(IO_3)_4,2KIO_3$, is formed as a brownish-violet, insoluble, crystalline powder when hydrated manganese dioxide is boiled with iodic acid and potassium iodate.[3]

MANGANESE, SULPHUR AND SELENIUM.

522 *Manganese Monosulphide*, MnS, occurs as the mineral manganese blende, or alabandite, forming a steel-grey, crystalline mass with a green streak, and sometimes observed in cubes

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[1] *Bull. Soc. chim.*, 1914, [4], **15**, 273, 408.

[2] Kuznetzoff, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 290.

[3] Berg, *Compt. rend.*, 1899, **128**, 673.

and octahedra. It has a specific gravity of 4·04, and occurs in veins in the coal mines in Transylvania, and in Freiberg and Mexico. It may be obtained artificially in the form of a dark grey powder, which melts at a high temperature, forming a steel-grey, crystalline mass, by heating the monoxide, the carbonate, or the sulphate in a current of hydrogen sulphide (Arfvedson), or in green octahedra by heating manganous sulphide with a little sulphur in the electric furnace.[1] Ammonium sulphide and the other monosulphides of the alkali metals precipitate anhydrous manganese sulphide from a solution of a manganous salt in the form of a light flesh-coloured precipitate, which dissolves readily in dilute acids and oxidises on exposure to the air, assuming a brown tint. When left in contact with ammonium sulphide, or heated to 300°,[2] and when suspended in a dilute solution of sulphuretted hydrogen and exposed to a low temperature, it passes into the green, crystalline sulphide.[3] According to Olsen and Rapalje a grey form of the sulphide also exists and the sulphide precipitated by ammonium sulphide is a mixture of this and a red form. The sulphide precipitated by sodium sulphide does not contain the grey form,[4] and does not become green in contact with excess of the precipitant.

Manganese sulphide combines with the sulphides of the alkali metals to form salts.[5] The dark-red, crystalline potassium salt, $K_2S,3MnS$, is formed when anhydrous manganese sulphate is gradually heated to redness with three parts of potassium carbonate, 0·2 part of lamp-black, and excess of sulphur.

Manganese Disulphide, MnS_2.—This substance is found as the mineral hauerite in crystals belonging to the regular system. They possess a metallic, adamantine lustre, and a reddish-brown colour, and occur in clay at Kalinka in Hungary, together with sulphur and gypsum.

Manganous Sulphate, $MnSO_4$, is best prepared by mixing commercial black oxide of manganese to a paste with sulphuric acid and heating the mixture in a crucible to strong redness, when the greater part of the iron sulphate is destroyed. The filtrate obtained after lixiviating the residue is then heated with a small quantity of manganous carbonate in order to precipitate the last traces of iron.

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[1] Mourlot, *Compt. rend.*, 1895, **121**, 202.

[2] Antony and Donnini, *Gazz.*, 1893, **23**, i., 560.

[3] Villiers, *Compt. rend.*, 1895, **120**, 322; see also Hahn, *Zeit. anorg. Chem.*, 1922, **121**, 209.

[4] *J. Amer. Chem. Soc.*, 1904, **26**, 1615, where the literature is quoted.

[5] Völker, *Annalen*, 1846, **59**, 35; Brunner, *Arch. sci. phys. nat.*, 1889, **22**, 68.

It has a specific gravity of 3·1, and is decomposed at a bright red heat, leaving a residue of red oxide of manganese. Manganous sulphate forms a number of hydrates and the equilibrium curve for this substance and water is one of great complexity. Below 8°, the heptahydrate separates out, between 8° and 27° the pentahydrate is the stable form, and above 27° the monohydrate. The solubility of the latter decreases as the temperature rises, so that a maximum of solubility exists at 27°. In addition to these stable forms, several labile hydrates exist, the most important of these being the tetrahydrate, which separates at about 30° in rose-coloured prisms of sp. gr. 2·097 (Kopp). Several other hydrates have been described, but it is doubtful whether they all exist.[1] One hundred parts of water dissolve:

At	0°	9°	15°	27°	50°	70°	100°
$MnSO_4$	53·2	59·3	61·1	66	59·5	52	33·2 parts.

The last trace of water is expelled from the monohydrate only at 450°.

Manganous sulphate is insoluble in absolute alcohol, this liquid removing a portion of the water from the hydrates. Finely crystalline double sulphates[2] of the isomorphous series, $R^I_2SO_4,R^{II}SO_4,6H_2O$, are formed when manganous sulphate and the alkali sulphates are crystallised together.

Manganous Aluminium Sulphate, $MnSO_4,Al_2(SO_4)_3,24H_2O$.—This substance occurs as the mineral apjohnite found in Algoa Bay in South Africa.[3]

Manganic Sulphate, $Mn_2(SO_4)_3$.—Manganic oxide and hydroxide dissolve with difficulty in sulphuric acid. The red oxide, Mn_3O_4, on the other hand, dissolves readily, yielding a purple-red solution. If the finely divided precipitated dioxide is treated with sulphuric acid, oxygen is evolved, and at a temperature of 138° a green liquid is obtained from which the sulphate is precipitated as a non-crystalline powder. In order to purify this salt it is brought on to a porous porcelain plate, when the greater part of the sulphuric acid is absorbed; the residue is then washed with pure nitric acid, the salt dried in absence of air on another plate, and then heated to 150°.[1]

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[1] Schieber, *Monatsh.*, 1898, **19**, 280; Cottrell, *J. Physical Chem.*, 1900, **4**, 637; Richards and Fraprie, *Amer. Chem. J.*, 1901, **26**, 75.

[2] See also Scott, *Journ. Chem. Soc.*, 1897, **71**, 567; Mallet, *ibid.*, 1900, **77**, 221; 1902, **81**, 1549.

[3] *Phil. Mag.*, 1856, [3], **12**, 103.

Manganese Alums.—Manganese forms a series of alums, $R^I_2SO_4,Mn_2(SO_4)_3,24H_2O$, which crystallise in pink or red, octahedral forms. They are decomposed by water, but are stable in a solution of 1 volume of sulphuric acid diluted with 3 of water, provided that the temperature is kept low. The potassium and ammonium salts are extremely unstable and have not been obtained pure, but the cæsium and rubidium salts can be prepared. The salts obtained by the addition of the sulphates of potassium and ammonium to manganic sulphate and evaporating are not true alums, but contain less water of crystallisation.[2] An anhydrous ammonium manganic sulphate has also been obtained and forms violet crystals which are decomposed by water.[3]

Manganic Cæsium Alum, $Cs_2SO_4,Mn_2(SO_4)_3,24H_2O$, may be prepared by dissolving cæsium sulphate and manganic acetate, $Mn_2(C_2H_3O_2)_6$ (obtained by the action of potassium permanganate on manganous acetate dissolved in glacial acetic acid), in dilute sulphuric acid and cooling to –20° (Christensen). It can be obtained also by electrolysing at 10–15° a solution of manganous sulphate and cæsium sulphate in dilute sulphuric acid placed in the anode compartment of an electrolytic cell.[4] It forms coral-red crystals of the regular system (class 30, p. 209) and is decomposed by water. It melts at 40° in its water of crystallisation.

The *Rubidium Alum* closely resembles the cæsium salt, but decomposes at about 15°, whilst the potassium and ammonium alums decompose at still lower temperatures (Christensen).

Manganese Dioxysulphate or Persulphate, $Mn(SO_4)_2$, was first prepared by Fremy,[5] and can best be obtained by oxidising manganous sulphate in warm sulphuric acid with the calculated quantity of potassium permanganate. When the solution is sufficiently concentrated, it is precipitated in the form of black crystals, which are soluble in sulphuric acid, forming a brown solution which is stable up to 80°, but above that temperature decomposes with the formation of manganic sulphate. On diluting the solution the salt is hydrolysed and manganese dioxide is precipitated. Electrolysis[1] of a solution of manganese sulphate in sulphuric acid yields a solution of it, which, however, is not free from manganic sulphate. It has been used as an oxidising agent in organic chemistry.

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[1] Carius, *Annalen*, 1856, **98**, 53.

[2] Christensen, *Zeit. anorg. Chem.*, 1901, **27**, 328.

[3] Lepierre, *Compt. rend.*, 1895, **120**, 924.

[4] Piccini, *Zeit. anorg. Chem.*, 1898, 17, 355; 1899, **20**, 12.

[5] *Compt. rend.*, 1876, **82**, 475, 1231.

Manganous Dithionate, $MnS_2O_6,3H_2O$.—This salt is of interest inasmuch as it is employed for the preparation of dithionic acid (Vol. I., p. 459). It is obtained by passing sulphur dioxide through water in which finely divided manganese dioxide is suspended. The solution always contains a small quantity of manganous sulphate, and for this reason baryta water is added as long as a precipitate of barium sulphate is formed. Manganous dithionate forms easily soluble rhombohedral crystals.

Double *selenates* of manganese with potassium, rubidium, cæsium and ammonium have been prepared.[2]

MANGANESE AND THE ELEMENTS OF THE NITROGEN GROUP.

523 *Manganese Nitride,* Mn_3N_2.—Nitrogen reacts vigorously with manganese at a red heat to produce this compound. It is a dark coloured powder, which yields ammonia when heated in hydrogen or fused with potash, and is attacked only with difficulty by acids.[3]

Manganous Nitrate, $Mn(NO_3)_2$.—The hydrate with $6H_2O$ crystallises with difficulty in colourless, deliquescent needles which melt at 25·8°, and are readily soluble in alcohol. A hydrate with $3H_2O$ also exists[4] which is stable above 25° and melts at 35·5°. The nitrate decomposes at 129·5°, at which temperature a black deposit of manganese oxides is formed.

Manganese Phosphides.—The freezing points of manganese–phosphorus mixtures have been determined by Żemcżwżnyj and Efremow[5]: these prove the existence of two compounds. The first has the formula Mn_5P_2, the second probably has the formula MnP. The substance Mn_3P_2, described by many of the earlier workers, is really a eutectic mixture. The magnetic properties of the compound Mn_5P_2 have been studied by Wedekind and Veit.[6]

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[1] *Zeit. Elektrochem.*, 1905, 11, 853.

[2] Tutton, *Proc. Roy. Soc.*, 1922, [*A*] 101, 225.

[3] Prelinger, *Monatsh.*, 1894, 15, 391; Haber and van Oordt, *Zeit. anorg. Chem.*, 1905, 44, 341; Shukow, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 457.

[4] Funk, *Ber.*, 1899, 32, 96.

[5] *Zeit. anorg. Chem.*, 1908, 57, 241.

[6] *Ber.*, 1907, 40, 1268.

Manganous Phosphates.—These salts have been investigated by Heintz,[1] Debray,[2] Bödecker,[3] and Erlenmeyer.[4] The normal manganous orthophosphate, $Mn_3(PO_4)_2,7H_2O$, is a white, imperfectly crystalline precipitate. The *monohydrogen salt*, $HMnPO_4,3H_2O$, forms small, prismatic, rose-coloured, rhombic crystals slightly soluble in water, and the *dihydrogen phosphate*, $H_4Mn(PO_4)_2,2H_2O$, crystallises in red, four-sided prisms which deliquesce on exposure to the air, decomposing into free phosphoric acid and the preceding salt.[5]

Manganous salts are precipitated by ammonium phosphate as *manganous ammonium phosphate*,[6] $Mn(NH_4)PO_4,H_2O$, which is converted by ignition into the *pyrophosphate*, $Mn_2P_2O_7$.

Manganic Phosphates.—Both manganic oxide and the dioxide dissolve in a concentrated solution of phosphoric acid, in the latter case with evolution of oxygen, with formation of a deep violet liquid, from which a violet-coloured, crystalline mass separates out (Gmelin). This decomposes in contact with water, and manganic hydroxide is precipitated from the solution by alkalis. On evaporating the red solution a peach-blossom-coloured powder separates, consisting of manganic metaphosphate, $Mn(PO_3)_3,H_2O$.[7] The normal phosphate $MnPO_4,H_2O$, an acid pyrophosphate, $MnHP_2O_7$, and the salts $MnKP_2O_7$ and $Mn_4P_6O_{21},14H_2O$,[8] have also been prepared.[9]

Manganese Arsenides.—Two arsenides of manganese are known,[10] the first of which, MnAs, is non-magnetic, but is converted by heating into the magnetic compound, Mn_2As.

Manganous Arsenate.—When arsenic acid is saturated with manganese carbonate, a sparingly soluble salt having the composition $HMnAsO_4,H_2O$ is formed. This dissolves readily in arsenic acid with formation of the salt $H_4Mn(AsO_4)_2$, which latter crystallises in rectangular plates. Several double salts with the alkali arsenates are also known.[11]

[1] *Pogg. Ann.*, 1848, **74**, 450.

[2] *Ann. Chim. Phys.*, 1861, [3], **61**, 433.

[3] *Annalen*, 1849, **69**, 208.

[4] *Annalen*, 1877, **190**, 191.

[5] See also Viard, *Compt. rend.*, 1899, **129**, 412.

[6] Dakin, *Zeit. anal. Chem.*, 1900, **39**, 784.

[7] Hermann, *Pogg. Ann.*, 1848, 74, 303. See also Barbier, *Compt. rend*, 1902, **135**, 1054, 1109.

[8] Auger, *Compt. rend.*, 1901, **133**, 94.

[9] Christensen, *J. pr. Chem.*, 1883, [2], **28**, 1; Schjerning, *J. pr. Chem.*, 1892, [2], **45**, 515.

[10] Wedekind, *Zeit. Elektrochem*, 1905, **11**, 850; *Ber. deutsch. physik. Ges.*, 1906, **4**, 412. Schoen, *Metallurgie*, 1911, **8**, 739.

[11] Lefèvre, *Compt. rend.*, 1890, **110**, 405.

Manganese Antimonides.—Two compounds, Mn_2Sb and Mn_3Sb_2, exist,[1] and can be prepared by heating the elements in the right proportions; the former is strongly, the latter only weakly magnetic.

MANGANESE AND BORON.

524 *Manganese Diboride*, MnB_2, is produced when a mixture of manganese thermite and boron is ignited or the oxide reduced with boron, and may be purified by treatment with chlorine. It forms grey-black crystals, which, when pure, are non-magnetic, decompose in warm water, and dissolve in concentrated acids.[2]

Manganese Monoboride, MnB, is prepared by the reduction of red oxide of manganese with boron at a white heat in a magnesia crucible, or by the direct union of its elements, and forms a black, crystalline powder of specific gravity 6·2, which resembles the diboride in its properties, but is strongly magnetic and dissolves more readily in acids.[3]

Manganese borate is used in the preparation of drying oils and oil varnishes[4]; it is made by adding manganous sulphate to a solution of borax, washing and drying the precipitate. It is a mixture of varying composition, not a definite compound.[5] The compounds $Mn(BO_2)_2$ and MnB_4O_7 have been prepared by melting manganese oxide or carbonate with boron trioxide.[6]

MANGANESE AND THE ELEMENTS OF THE CARBON GROUP.

525 *Manganese Carbide*, Mn_3C, is formed when red oxide of manganese is heated with charcoal or calcium carbide in the electric furnace. It has the specific gravity 6·89, and with water yields equal volumes of hydrogen and methane:

$$Mn_3C + 6H_2O = CH_4 + H_2 + 3Mn(OH)_2.$$

It burns readily in oxygen, and is easily attacked by fluorine and chlorine.[7] When very strongly heated it dissociates, the manganese volatilises, and the carbon remains as graphite.[8]

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[1] Williams, *Zeit. anorg. Chem.*, 1907, **55**, 1.

[2] Wedekind, *Ber.*, 1905, **38**, 1228; Wedekind and Fetzer, *Ber.*, 1907, **40**, 1264; Binet du Jassonneix, *Ber.*, 1907, **40**, 3193.

[3] Binet du Jassonneix, *Compt. rend.*, 1904, **139**, 1209; 1906, **142**, 1336.

[4] Hartley and Ramage, *Journ. Chem. Soc.*, 1893, **63**, 129.

[5] See Endemann and Paisley, *Zeit. angew. Chem.*, 1903, **16**, 175.

[6] Guertler, *Zeit. anorg. Chem.*, 1904, **40**, 244.

[7] Moissan, *Compt. rend.*, 1896, **122**, 421; 1897, **125**, 839.

[8] Gin and Leleux, *Compt. rend.*, 1898, **126**, 749.

Manganese Carbonate, $MnCO_3$, occurs in the pure state in the rose-red crystals of manganese spar, rhodochrosite or dialogite, and also as an isomorphous mixture with chalybite. These minerals crystallise, like calc-spar, in rhombohedra, but manganocalcite, $(Mn,Ca,Mg)CO_3$, is isomorphous with aragonite.

Hydrated manganese carbonate is obtained as a white precipitate by mixing a solution of the chloride or sulphate of manganese with sodium carbonate. In the moist state it soon becomes brown-coloured on exposure to the air; it dissolves in 8,000 parts of pure water, and in about half this quantity of water saturated with carbon dioxide.

Manganese and Cyanogen.—When a concentrated solution of manganese acetate is warmed with solid potassium cyanide a green precipitate is thrown down of $KCN,Mn(CN)_2$; this gradually disappears, and in its place dark blue crystals of *potassium manganocyanide*, $K_4Mn(CN)_6,3H_2O$, are formed.[1] The manganocyanide is obtained also when manganous carbonate is heated to a temperature of from 40° to 50° with a solution of potassium cyanide.[2] The salt crystallises in deep violet-blue, efflorescent, tetragonal tablets. Its solution oxidises on exposure to air with formation of *potassium manganicyanide*, $K_3Mn(CN)_6$, which crystallises in dark-red prisms. This latter salt when brought into contact with potassium amalgam in aqueous solution is again transformed into manganocyanide. The constitution of these complex salts will be referred to under the corresponding iron compounds.

Manganese Thiocyanate, $Mn(SCN)_2$, may be prepared from manganous sulphate and barium thiocyanate. The anhydrous salt is yellow, and forms a green hydrate with $3H_2O$, which crystallises at the ordinary temperature. Concentrated aqueous solutions are green, but become pink when they are diluted.[3]

Manganese Silicides.—Some doubts exist as to the number of definite compounds formed by these elements. A study of the freezing-point curve for mixtures of the two[4] indicates the existence of the two compounds, Mn_2Si and $MnSi$. The compounds $MnSi_2$[5] and Mn_3Si_2[6] have also been described.

The silicide, Mn_2Si, is formed when the two elements are heated together in the electric furnace,[1] by firing a mixture of silica, manganese oxide, and aluminium, or by heating a mixture of potassium silicofluoride, red oxide of manganese, copper, and sodium (Lebeau). It is a very hard, brittle mass, which has a metallic lustre and steel-grey colour and a specific gravity of 6·4. It is not decomposed by water at the ordinary temperature, but it is attacked by steam, oxygen, or chlorine at a red heat, and dissolves in hydrochloric acid. Fluorine decomposes it at the ordinary temperature.

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[1] Eaton and Fittig, *Annalen.*, 1868, 145, 157.

[2] Descamps, *Ann. Chim. Phys.*, 1881, [5], 24, 178.

[3] Kumakoff. Quoted by Grossmann, *Ber.*, 1905, 37, 559.

[4] Doerinckel, *Zeit. anorg. Chem.*, 1906, 50, 117.

[5] De Chalmot, *Amer. Chem. J.*, 1896, 18, 536.

[6] Gin, *Compt. rend.*, 1906, 143, 1229.

The *monosilicide*, MnSi, forms hard, lustrous, tetrahedral crystals of specific gravity 5·9, whilst the *disilicide*, $MnSi_2$, forms dark-grey, octahedral crystals of specific gravity 5·24. The compound described by Gin of the formula Mn_3Si_2 is probably impure Mn_2Si (Lebeau).[2]

Manganous Silicates occur as isomorphous constituents of many minerals, and some naturally occurring manganese silicates are also known. Thus, for instance, rhodonite, $MnSiO_3$, occurs in light brownish-red, transparent, triclinic crystals, and tephroite, Mn_2SiO_4, crystallises in the tetragonal system in rose-red, brown, or grey masses, and usually occurs together with rhodonite.

DETECTION AND ESTIMATION OF MANGANESE.

526 Manganese is distinguished by forming a flesh-coloured sulphide readily soluble in dilute acids. In the course of analysis manganese is thrown down with the sulphides and hydroxides of the metals which are precipitated by ammonium sulphide. If the precipitate be treated with very dilute cold hydrochloric acid, the sulphides of cobalt and nickel, if present, remain undissolved. The solution is heated in order to remove the sulphuretted hydrogen, oxidised with potassium chlorate, and an excess of caustic soda is added. Iron, manganese, and uranium are thus thrown down as hydroxides. The washed precipitate is then dissolved in hydrochloric acid, the liquid neutralised, and ammonia and ammonium chloride are added, when the whole of the metals, with the exception of manganese, are thrown down; the filtrate is then evaporated to dryness, and the residues heated to get rid of ammonium salts. The mass which

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[1] Vigouroux, *Compt. rend.*, 1895, **121**, 771; 1905, **141**, 722; Lebeau, *Compt. rend.*, 1903, **136**, 89, 231; *Bull. Soc. chim.*, 1903, [3], **29**, 797; *Ann. Chim. Phys.*, 1904, [8], **1**, 553.

[2] *Compt. rend.*, 1907, **144**, 85.

remains can be treated in various ways for the detection of manganese. The simplest plan is to fuse a small quantity of the residue with caustic soda and saltpetre, when the dark-green potassium manganate is formed, and this colour becomes deep blue on cooling. It dissolves in water with a green colour, which on addition of a little nitric acid turns red. Other characteristic reactions for the manganese salts are the following. Potash and soda precipitate the white hydroxide, which soon becomes brown on exposure to air. Ammonia in the presence of ammonium chloride produces no immediate precipitate, but the solution rapidly absorbs oxygen from the air, brown manganic hydroxide being deposited. When a manganese compound is fused with borax an amethyst-coloured bead is obtained in the outer flame, and this in the inner flame becomes colourless.

The non-luminous gas flame is coloured green by manganese chloride, and this exhibits a spectrum in which the lines in the green and yellow are :[1] 5587(α), 5392(β), and 5195(γ). The spark spectrum of manganese contains a large number of bright lines, of which the most important are : 6022, 6017, and 6014 in the orange; 4824 and 4784 in the green; 4766, 4762, and 4754 in the blue; 4235 and 4228 in the indigo (Lecoq de Boisbaudran).

The absorption spectrum of permanganic acid and its potassium salt exhibits in very dilute solution five distinct bands; a more concentrated solution gives continuous absorption in the yellow and green; and this is observed also in certain solutions of manganic salts. The latter, however, do not show the bands on dilution. The manganous salts also show a characteristic absorption spectrum, chiefly in the ultra-violet.[2]

In order to estimate manganese gravimetrically it may be precipitated as the carbonate or, by the action of bromine water and ammonia or nitric acid and a chlorate, as the dioxide. These are both converted by ignition to the red oxide, Mn_3O_4, in which condition the manganese may be weighed; a better method is to ignite the precipitate, dissolve it in sulphuric acid, drive off excess of acid, and weigh as the sulphate, $MnSO_4$. Manganese may also be precipitated as the sulphide, and either weighed in this form by Rose's method, or converted to the oxide by ignition, or to the sulphate. It may be precipitated as ammonium manganese phosphate and weighed as the pyrophosphate, $Mn_2P_2O_7$. Electrolytic methods have been proposed.

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[1] Hoppe-Seyler, *J. Chem.*, 1870, 110, 203.

[2] Lambert, *Compt. rend.*, 1905, 141, 357.

Manganese always occurs in nature together with iron. In order to separate these the solution is heated with ammonium chloride, neutralised with the requisite quantity of ammonia, and the iron precipitated with ammonium acetate. The manganese can then be estimated in the filtrate in the above way. An equally accurate method, but easier and more rapid, is to remove the iron by precipitation with "cupferron."[1]

Manganese may be estimated volumetrically by titration with potassium permanganate in presence of zinc sulphate (p. 1190), or by conversion into permanganate, which is then estimated by titration with standard oxalic acid, hydrogen peroxide, or some other reducing agent. When small quantities are concerned this is best done by boiling the manganese salt with concentrated nitric acid, solid lead peroxide, and a little dilute sulphuric acid, and filtering the resulting liquid through asbestos, or by digesting the salt with nitric acid and sodium bismuthate, or a persulphate, sulphuric acid, and silver nitrate.

Manganese may also be precipitated as the hydrated dioxide by boiling with dilute sulphuric acid and ammonium persulphate, and the dioxide either estimated volumetrically, or in the absence of other metallic salts, gravimetrically by conversion into the red oxide.[2]

Very small traces of manganese can be detected and estimated colorimetrically by oxidising it to permanganate and comparing its colour with potassium permanganate solutions of known concentration.[3]

Valuation of Manganese Ores.—The most accurate and convenient methods for the estimation of the quantity of manganese dioxide in manganese ores are those of Bunsen,[4] and of Fresenius and Will.[5] By the former method, the quantity of chlorine evolved on treatment with hydrochloric acid is directly determined. The gas is collected in a solution of potassium iodide, and the liberated iodine estimated with a dilute solution of sulphurous acid or sodium thiosulphate.

Fresenius and Will's method depends upon the action:

$$MnO_2 + C_2O_2(OH)_2 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O,$$

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[1] See Fresenius, *Zeit. anal. Chem.*, 1911, **50**, 35.

[2] von Knorre *Zeit. angew. Chem.*, 1901, **14**, 1149.

[3] See Marshall, *Chem. News*, 1904, **89**, 76.

[4] *Journ. Chem. Soc.*, 1856, **8**, 219.

[5] *Annalen*, 1843, **47**, 87.

i.e. 88·00 parts of carbon dioxide correspond to 86·93 parts of manganese dioxide. The reaction is carried out in a weighed apparatus provided with a drying tube, the loss of weight being ascertained.

Another method, based on the same reaction, is to start with a known amount of oxalic acid and to determine the excess of this, after the manganese dioxide has been reduced, by titration with standard potassium permanganate.

The Atomic Weight of manganese has been determined by several chemists, among the earliest of whom were Berzelius,[1] Dumas,[2] and V. Hauer.[3] Dewar and Scott, by estimating the percentage of silver in silver permanganate, obtained 55·01;[4] and Marignac, by converting pure MnO into $MnSO_4$, obtained 55·02.[5] Baxter and Hines from the analysis of the bromide and chloride have found 54·96.[6] The value at present (1922) adopted is 54·93.

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[1] *Pogg. Ann.*, 1828, **14**, 211.

[2] *Annalen*, 1860, **113**, 25.

[3] *Wien Akad. Ber.*, 1857, **25**, 124.

[4] *Proc. Roy. Soc.*, 1883, **35**, 44.

[5] *Zeit. anal. Chem.*, 1884, **23**, 123.

[6] *J. Amer. Chem. Soc.*, 1906, **28**, 1560.

GROUP VIII.

Sub-group (*a*) Iron, Cobalt, Nickel.
" (*b*) Ruthenium, Rhodium, Palladium.
" (*c*) Osmium, Iridium, Platinum.

527 The metals placed by Mendeléev in the eighth vertical group form a very remarkable feature of his arrangement of the elements. They occur in three sub-groups, each containing three metals, forming the termination of the even horizontal series 4, 6, and 10, each group being the connecting link between the elements of the even series which precedes and those of the odd series which follows. The three metals which make up each horizontal sub-group resemble one another very closely, and differ much less in atomic weight, atomic volume, and general physical properties than is usual in the successive elements of a horizontal series, as may readily be seen by a reference to Lothar Meyer's diagram (p. 62).

This remarkable similarity is borne out by the chemical behaviour of these elements, the various platinum metals, for example, being so similar that their separation from each other is a matter of the greatest difficulty, and this is true also of cobalt and nickel.

At the same time, a certain degree of similarity can be traced between those metals which are in the same vertical column, more particularly in sub-groups *b* and *c*. Thus ruthenium and osmium, rhodium and iridium, palladium and platinum agree very closely in many of their most characteristic properties, such, for example, as the formation of a tetroxide, which is peculiar to ruthenium and osmium, etc.

From the analogy of the preceding groups, it would be expected that the characteristic oxide of the metals of this group would have the formula MO_4 or M_2O_8. Actually, however, only ruthenium and osmium form such an oxide, and this is not an acidic oxide, whilst all the metals of the group form lower oxides, many of which correspond to series of stable salts.

All these metals, unlike the other members of the even series of the periodic system, form metallo-organic compounds.[1]

A very characteristic property of the metals of this group is their tendency to form complex radicles with other elements or groups, which then act as basic or acidic radicles, and thus give rise to extended series of compounds. These substances, as a rule, differ entirely in properties from the ordinary salts of the metal, this being due to the fact that each radicle has its own characteristic properties, and those of the metal appear only when the radicle has been broken up. Some of the most important of these complex derivatives are the double cyanides, such as the ferrocyanides and their analogues, the complex halogen derivatives of the platinum metals, the ammoniacal derivatives of cobalt and of the platinum metals, the double nitrites, sulphites, etc. This tendency is shared by chromium and to some extent by manganese, copper, and other metals which either immediately precede or follow the metals of Group VIII in the periodic system.

SUB-GROUP (*a*). THE IRON GROUP.

Iron, Cobalt, Nickel.

528 These three metals are all magnetic, melt at a high temperature, are oxidised when strongly heated in air or oxygen, and decompose steam at a red heat. They all form basic oxides of the formula $M^{II}O$, and a corresponding series of coloured salts in which the metal is divalent. The sesquioxides $M^{III}_2O_3$ also act as basic oxides, but the corresponding salts of nickel and cobalt are so unstable that they speedily decompose with formation of salts corresponding to the lower oxide. Those of iron, on the other hand, are much more stable, and are formed from those of the lower oxide on exposure to the air. These metals, moreover, all yield oxides of the formula M_3O_4, to which no stable salts correspond, and which are probably to be considered as being themselves salts of the formula $M^{II}M^{III}_2O_4$. Cobalt, in addition to these, probably forms an unstable acidic dioxide, whilst derivatives of the corresponding nickel oxide are also known, but no such derivatives of iron have been prepared, although the corresponding sulphide exists as iron pyrites. Iron,

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[1] Pope and Peachey, *Proc. Chem. Soc.*, 1907, **23**, 86.

however, forms a series of compounds known as the ferrates, which are derived from a hypothetical acidic trioxide, FeO_3, to which no analogue is known among the compounds of nickel and cobalt.

Nickel and iron both unite with carbon monoxide to form volatile liquids, whereas cobalt forms a crystalline carbonyl.

Nickel has much less tendency to form complex radicles than cobalt or iron, the most important of such derivatives formed by the last two being the cobaltammines and the cyanogen compounds of iron.

IRON (FERRUM). Fe = 55·84. At. No. 26.

529 Iron is the most important of all the metals. It seldom occurs in the metallic state in nature; the ores of iron are, however, found widely distributed. It is usually supposed that the iron age followed those of copper and bronze, although in many cases the art of working in iron became known at a very early period. It is, however, to be remembered that metallic iron is rapidly destroyed by rusting, at any rate in damp situations, and this may to some extent account for the comparatively rare occurrence of very early iron implements.

It appears probable that iron was first obtained from its ores in India, and it is certain that both the Assyrians and the Egyptians employed iron implements many centuries before our era. In the Pentateuch the metal iron is mentioned, as well as the furnaces in which it was prepared; the Hebrew name for iron, Barzél, is derived from the root Bazal, which signifies "to be hard," whilst the derivation of the Greek word *σίδηρος*, which occurs in Homer, is unknown. The Greeks obtained their iron from the Chalybes, a nation dwelling on the south coast of the Black Sea, from whom the Asiatic nations also obtained the metal. The Romans, on the other hand, procured their iron, not only from this district, but also from Spain, Elba, and Noricum. The Elban iron mines, which are to this day renowned for their fine specular iron, were worked by the Etruscans.

The word iron, which is identical with the Scandinavian "iarn" (instead of "isarn"), and with the German "Eisen" (adjective, "eisern"), appears to be connected with the Sanscrit "ayas" (Latin "aes"), and this, according to Grimm, is an indication that bronze was in use among the Germans at a much earlier date than iron. The alchemists connected iron with Mars, the god of war, and gave to it the sign ♂.

Native iron occurs, according to Andrews,[1] in small spiculæ distributed throughout the basalt of the Giant's Causeway, as well as in the old lavas of the Auvergne. The occurrence of terrestrial iron in large lumps has also been observed; these masses have, however, probably been formed in the firing of coal-pits when the burning mass has come in contact with ores of iron; the product is termed natural steel.

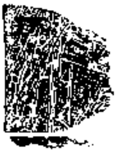

Fig. 191.

The native metal occurs more frequently in the form of *meteoric iron*. The meteorites falling in larger or smaller masses from extra-terrestrial sources may be divided into two groups: "Earthy meteorites," which consist chiefly of silicates, and "Meteoric irons," which consist of iron together with a larger or smaller quantity of nickel, the presence of this latter metal being characteristic of meteoric masses.[2] Meteoric iron likewise usually contains small quantities of cobalt and other metals, as well as graphite, ferrous sulphide, and schreibersite, $(Fe,Ni,Co)_3P$, this last compound being one which is not known to exist in any terrestrial mineral. When the surface of a meteoric iron is planed and polished, and then treated with dilute nitric acid, peculiar configurations make their appearance which were first noticed by Widmanstätten in the year 1808. These consist of rhombic folia or crystalline markings (shown in Fig. 191) which have a metallic lustre; the spaces enclosed by these markings are somewhat raised, so that a surface of meteoric iron thus treated may be used as a plate from which an engraving can be obtained. Similar structures have been artificially obtained in iron, steel and other alloys by slow cooling. Meteoric iron frequently occurs in considerable masses; thus, for instance, that which was discovered by Pallas in Siberia originally weighed 800 kilos. [analysis (*a*)], whilst that found in Bahia weighed nearly 7,000 kilos.; a still larger mass occurs at Chaco-Gualamba in Peru, which is said to weigh 16,000 kilos., and similar large masses have been found in other localities, both in North and South America, as well as in Africa. The largest known masses are those found at Ovifak on the Island of Disko, off Greenland, where fifteen blocks of meteoric iron occur, the weight of the two largest being, according to Nordenskjöld,[1] 21,000 and 8,000 kilos. [analysis (*b*)].

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[1] *Brit. Assoc. Reports*, 1852, 34.

[2] See Fletcher's *Introduction to the Study of Meteorites* (published by the Trustees of the British Museum, 1904). See also Prior, *Min. Mag.*, 1916, **18**, 26; 1920, **19**, 51.

The following table gives the composition of several meteoric irons:

Locality. Analyst.	(*a*) Siberia. Berzelius.	(*b*) Ovifak. Nordenskjöld.	(*c*) Brazil. Damover.	(*d*) Tennessee. J. L. Smith.
Iron	88·04	84·49	63·69	91·15
Nickel	10·73	2·48	33·97	8·01
Cobalt	0·46	0·07	1·48	0·72
Copper	0·07	0·27	0·05	0·06
Manganese	0·13	—	—	—
Carbon	0·04	10·62	0·02	—
Sulphur	trace	1·52	0·02	—
Phosphorus	—	0·20	0·05	—
Chlorine	—	0·72	—	—
Silicate	0·53	0·09	—	—
	100·00	100·46	99·28	99·94

Finely divided meteoric iron is constantly falling from extra-terrestrial space on to the earth: the occurrence of this meteoric dust has been observed in Sweden and in the snow-fields of Northern Siberia, the snow enclosing black magnetic particles which contain cobalt as well as iron. Similar particles of meteoric dust, consisting of metallic iron, have been found by Murray, of the *Challenger* expedition, at great depths in mid-ocean. It is only under conditions such as the above that it is possible to detect this fine meteoric dust, in consequence of the enormous accumulation elsewhere of terrestrial dust.

530 Iron is usually found in combination either with oxygen or sulphur. Of the large number of minerals which contain iron only those will now be mentioned which occur most commonly and in the largest quantity; the ores will be specially described hereafter. The most important oxygen compounds of iron are red hæmatite, or specular iron ore, Fe_2O_3; brown hæmatite, $2Fe_2O_3,3H_2O$; magnetic iron ore, Fe_3O_4; spathic iron ore, $FeCO_3$, the latter containing other isomorphous carbonates. Again, iron pyrites, FeS_2, occurs largely, whilst magnetic pyrites, Fe_7S_8, is less common; iron sulphide also forms an important constituent of copper pyrites, $CuFeS_2$, arsenical pyrites, FeAsS, and other minerals. Silicates of iron are found in most geological

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[1] *Pogg. Ann.*, 1874, 151, 154.

formations, and from these iron oxide finds its way into the soil, in which it is usually present in considerable quantity, imparting to it a reddish or brown colour. This fact was known to Pliny, who mentions that the presence of iron may be recognised by the colour of the soil. Iron compounds are contained in solution in spring- and river-waters, as well as in the water of the ocean, and it is from one or other of these sources that plants obtain the iron which forms an essential constituent of their chlorophyll.

In 1702 N. Lemery proved that the ashes of plants contained iron: this observation was confirmed by the experiments of Geoffroy in 1705, who, however, assumed that the iron was not originally contained in the plants, but that it was produced when they were burned. Other celebrated chemists, such as Becher, held the view that the iron which made its appearance when certain substances were subjected to chemical treatment was not contained in them, but was produced independently. This erroneous opinion was first disproved by Lemery.

Iron likewise is a necessary constituent of the animal body; for instance, hæmoglobin, the red colouring matter of the blood, contains 0·336 per cent. of iron. Iron preparations have also long been employed as medicine, especially in anæmia. After the use of iron the number of red corpuscles is increased, and the amount of hæmoglobin which they contain becomes larger. The presence of iron in the blood was first shown by Menghini of Bologna in 1747.

The existence of iron in large quantities in meteoric masses indicates a wide cosmical distribution of the element, and this conclusion has been confirmed by spectrum analysis, which indicates the presence of iron in the sun and many fixed stars.

531 *Preparation of Pure Iron.*—Iron is usually produced from its oxides by reduction with carbon, and is thus obtained on the large scale; thus prepared, however, iron is not pure, but contains carbon. In order to obtain chemically pure iron, the oxide, or oxalate, may be heated in a current of hydrogen at the lowest possible temperature; the metal is obtained by this process as a black powder which oxidises and becomes incandescent in the air; if the reduction is carried on at a higher temperature the powdered iron is not pyrophoric. Reduction at 1000° of the oxide or basic nitrate made by heating very carefully purified ferric nitrate gives a product with a distinct metallic lustre and a light grey colour. The iron thus obtained is of exceptional purity and is remarkably inert.[1]

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[1] Lambert and Thomson, *Journ. Chem. Soc.*, 1910, **97**, 2430.

Pure iron may be prepared also by electrolysis;[1] this process has received considerable attention during recent years and deposits containing 99·98 per cent. of iron have been obtained. Two solutions from which satisfactory deposits can be obtained have been used on an industrial scale. One consists of a highly concentrated solution of ferrous and calcium chlorides, which is used at a temperature between 90° and 110° with a current density of 180 amperes per square foot of cathode area. The other solution consists of a concentrated solution of ferrous and sodium sulphates; it is used at a temperature near the boiling point with a high current density. Electrolytic deposition has also been used for making up worn surfaces of machinery to correct gauge.

Properties.—Pure iron has a specific gravity of 7·86, possesses an almost silver-white lustre, and takes a high polish; it is, with the exception of cobalt and nickel, the most tenacious of all the ductile metals at the ordinary temperature, but becomes brittle at the temperature of liquid air.[2] Its average specific heat over 15–100° is 0·10983, but this increases somewhat rapidly with the temperature up to 850°, after which it decreases.[3]

Pure iron becomes soft at a red heat, and may be readily welded at a white heat, but above the welding point it becomes brittle under the hammer. It fuses less readily than commercial wrought iron, the melting point being 1505–1520°,[4] and when heated in the electric furnace it readily distils, much frothing taking place in the boiling liquid owing to the evolution of occluded gases.[5] It is attracted by the magnet and may also be rendered magnetic, but loses this property rapidly. Carbonised iron or steel, on the other hand, retains its magnetic property at the ordinary temperature, but loses it at a red heat.

When iron is heated from the ordinary temperature to the melting point, it undergoes three changes. These changes are accompanied by an absorption of heat and the curve of heating exhibits corresponding breaks. Similarly, when molten iron is cooled, these changes occur in the reverse order, accompanied by evolution of heat, and the cooling curve exhibits similar breaks. Owing to an inertia on the part of the iron to undergo these changes, the temperature at which each occurs is different according as the metal is heated or cooled; the breaks on the cooling curve are slightly lower than the corresponding ones on the heating curve. The explanation of these changes lies in the fact that iron exists in four allotropic forms,[1] distinguished as α-, β-, γ- and δ-iron (ferrite), though some regard the β-modification as a solid solution of γ- in α-ferrite.[2] The α-form, which is the sole constituent of pure soft iron and is capable of assuming magnetic properties, is stable from the ordinary temperature up to about 760°, when the first change occurs, coinciding with the disappearance of magnetic properties; the β-form is stable from this point up to about 900°, when the second change takes place; the γ-form, which is the variety usually formed on solidification of the fused metal, is stable from this to about 1400°, when the third change occurs; the δ-form is stable from here to the melting point (1505°). The α-, β-, and γ-forms all crystallise in the regular system; the α- and β-forms possess a space-centred and the γ-form a face-centred cubic lattice.[3]

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[1] Maximowitsch, *Zeit. Elektrochem.*, 1905, **11**, 52; Ryss and Bogomolny, *ibid.*, 1906, **12**, 697. Compare Amberg, *ibid.*, 1908, **14**, 326; 1910, **16**, 125; Müller, *Metallurgie*, 1909, **6**, 145: Pfaff, *Zeit. Elektrochem.*, 1910, **16**, 217. Fischer and Guillet, *J. Iron and Steel Inst.*, 1914, **90**, 66; Hughes, *The Electrician*, 1920, **85**, 530.

[2] Dewar and Hadfield, *Proc. Roy. Soc.*, 1905, **74**, 326.

[3] Harker, *Phil. Mag.*, 1905, [6], **10**, 430.

[4] See Carpenter, *J. Iron Steel Inst.*, 1908, **78**, 290.

[5] Moissan, *Compt. rend.*, 1906, **142**, 425.

Iron combines readily with the elements of the chlorine group, and when strongly heated burns in oxygen, forming the magnetic oxide, and at a red heat decomposes steam with formation of the same oxide; it also burns at a red heat in sulphur vapour, and combines with carbon at a high temperature.

Iron readily occludes many gases, notably hydrogen, nitrogen, and the oxides of carbon. The solubilities of hydrogen and nitrogen in iron have been studied[4] and found to be proportional to the square root of the pressure of the gas. The solubility increases with temperature, and shows a marked alteration near the β-γ transition point, namely, at 930°. The excess of gas is liberated on cooling the molten metal, and that retained by the solid may be removed by heating it in vacuo.

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[1] Osmond and Cartaud, *Ann. des Mines*, 1901, **17**, 110; **18**, 113; *Compt. rend.*, 1906, **142**, 1530; **143**, 44; Ruer and Goerens, *Ferrum*, 1915, **13**, 1.

[2] Benedicks, *J. Iron Steel Inst.*, 1912, **86**, 242; *Eighth Inter. Cong. App. Chem.*, 1912, **22**, 13; Carpenter, *J. Iron Steel Inst.*, 1913, i., 315; Sauver, *J. Inst. Metals*, 1913, **88**, 171.

[3] Westgren and Lindh, *Zeit. physikal. Chem.*, 1921, **98**, 181; Westgren and Phragmén, *ibid.*, 1922, **102**, 1.

[4] Sieverts, *ibid.*, 1907, **60**, 129; Jurisch, *Stahl und Eisen*, 1914, **34**, 252.

Iron is also permeable to hydrogen. If an iron tube is immersed in acid [1] or used as cathode in electrolysis [2] the liberated hydrogen diffuses through the metal to the inside. Diffusion of molecular hydrogen through iron begins at about 350° and rapidly increases with temperature.[3] During its passage it combines with any sulphur, carbon, or phosphorus which may be present, thus removing them and rendering the iron soft.[4]

Iron dissolves in most dilute acids with evolution of hydrogen. Dilute nitric acid dissolves it in the cold without the evolution of any gas and with the formation of ferrous nitrate, $Fe(NO_3)_2$, and ammonium nitrate; when heat is applied, or when a stronger acid is employed, oxides of nitrogen are evolved, and ferric nitrate, $Fe(NO_3)_3$, is formed.

Passive Iron.—When iron is placed in concentrated nitric acid it appears to undergo a change, and is then not attacked by the acid.[5] It will then not precipitate metals, such as copper, from solutions of their salts, and is highly resistant to rusting. Iron in this state is termed "passive." This condition may be brought about by the action, not only of nitric acid, but also of other substances such as chloric, bromic, iodic, and chromic acids, and even hydrogen peroxide, as well as by electrolysis, the iron acting as anode in sulphuric acid solution.[6]

The cause of this phenomenon has not yet been definitely ascertained, and many suggestions have been made to account for it. It is possible that there are more kinds of passivity than one, and that no theory will cover all cases.[7] Schönbein, Faraday, and Beetz regarded it as due to the formation of a thin film of oxide on the surface of the iron, which protects it from further action, and this film, according to Haber and Goldschmidt,[7] possesses metallic conductivity.

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[1] Fuller, *Trans. Amer. Elect. Soc.*, **36**.

[2] Charpy and Bonnerot, *Compt. rend.*, 1912, **154**, 592; Fuller, *loc. cit.*

[3] Charpy and Bonnerot, *Compt. rend.*, 1913, **156**, 394; Bollati and Lussana, *Nuovo Cim.*, 1913, [6], **5**, i., 389. See also Smits, *Stahl und Eisen*, 1919, **39**, 3, 73, 406; Schmidt and Lücke, *Zeit. physikal. Chem.*, 1921, **98**, 152.

[4] Kier, *Phil. Trans.*, 1790, **80**, 359. See also Young and Hogg, *J. Physical Chem.*, 1915, **19**, 617.

[5] See Günther and Schulze, *Zeit. Elektrochem.*, 1912, **18**, 326; Flade and Koch, *Zeit. physikal. Chem.*, 1914, **88**, 307.

[6] Friend, *Journ. Chem. Soc.*, 1912, **101**, 50.

[7] *Zeit. Elektrochem.*, 1906, **12**, 49. See also Gordon and Clark, *J. Amer. Chem. Soc.*, 1906, **28**, 1534; Byers, *ibid.*, 1908, **30**, 1718; Krassa, *Zeit. Elektrochem.*, 1909, **15**, 490; Dunstan and Hill, *Journ. Chem. Soc.*, 1911, **99**, 1853.

Fredenhagen[1] supports the hypothesis that in the passive condition the iron is coated with a thin layer of gas, and points out that iron rendered passive by anodic polarisation has a different behaviour from that made passive by nitric acid, probably because the protective layer is oxygen in the one case, and nitric oxide in the other. Iron is readily rendered passive to a marked degree by nitrogen tetroxide and the presence of a film of this gas has also been suggested as the cause of passivity.[2] Hittorf,[3] Heathcote,[4] and Finkelstein,[5] on the other hand, regard the phenomenon as due to a chemical or electrical change taking place in the molecules forming the surface of the iron, the last-named author suggesting that ordinary iron consists of both ferrous and ferric iron molecules, and that by the action of the above substances the ferrous iron molecules are dissolved or converted into ferric molecules, which are not capable of attack by the reagents.[6] A similar idea is found in the theory of Smits,[7] who postulates two kinds of iron: a, base, and β, noble, which are in equilibrium. During anodic polarisation, or in nitric acid, the metal dissolves quicker than equilibrium can be established, and consequently there is produced on the surface an excess of β iron, the noble variety, so that the metal is resistant to attack or, in other words, is passive. Hydrogen (as also the halogens) tends to accelerate the change of β to a. During anodic polarisation or when the metal is dipped in nitric acid the hydrogen it contains is completely removed from the surface by oxidation. In either case, therefore, the passivity produced will persist until hydrogen diffuses from the interior of the metal to the surface, when the equilibrium is accelerated, the a variety being re-formed, and the metal becomes active again.

Lambert and Thomson[8] have prepared iron of exceptional purity and found it to be extremely resistant to chemical action, or, in other words, "passive." It would therefore appear that pure iron is passive,[9] and Lambert[10] has proposed the following definition of passivity: "The production by some chemical or electrochemical means of a physically homogeneous layer on the surface of a metal of which the surface was originally physically heterogeneous.

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[1] *Zeit. physikal. Chem.*, 1903, **43**, 1; 1908, **63**, 1.

[2] Young and Hogg, *loc. cit.* [3] *Zeit. physikal. Chem.*, 1900, **34**, 385.

[4] *Ibid.*, 1901, **37**, 368; *J. Soc. Chem. Ind.*, 1907, **26**, 899.

[5] *Ibid.*, 1902, **39**, 91.

[6] See also Smits and Lobry de Bruyn, *Proc. K. Akad. Wetensch. Amsterdam*, 1917, **19**, 880; Brown, *J. Phys. Chem.*, 1921, **25**, 429.

[7] *J. Soc. Chem. Ind.*, 1916, **35**, 928; *De Ingenieur*, 1915, 357. See also Smits, *The Theory of Allotropy* (Longmans), 1922, p. 342.

[8] *Journ. Chem. Soc.*, 1910, **97**, 2426.

[9] See also Flade and Koch, *Zeit. Elektrochem.*, 1911, **18**, 335.

[10] *Journ. Chem. Soc.*, 1915, **107**, 218.

Passive iron is rendered active again by chlorine, bromine, or iodine ions. Anodic polarisation by electrolysis of an iron salt can be made periodic by the addition of chlorine ions to the solution.[1]

Finely Divided or Reduced Iron (ferrum redactum) has long been used in medicine. *Spongy iron*, prepared by the reduction of burnt pyrites or other suitable iron ore, has been employed as filtering material for purifying water for domestic use.

532 *The Rusting of Iron.*—The formation of rust on exposed surfaces of iron was formerly supposed to be due to direct oxidation of the metal. However, contact with both air and water in the liquid state is necessary for the production of rust.[2] The investigations of Crace-Calvert[3] and Crum Brown[4] indicated that carbon dioxide, too, plays an essential part in the reaction, and in most cases of rusting it is certainly an active agent. The feebly acid solution of carbon dioxide in water attacks the iron with considerable rapidity, yielding a solution of ferrous carbonate or bicarbonate. This is then oxidised by the oxygen with formation of hydrated ferric oxide and evolution of carbon dioxide, which is thus available for further attack, its action therefore being catalytic:

$$\mathrm{Fe} + 2\mathrm{H_2O} + 2\mathrm{CO_2} = \mathrm{Fe(HCO_3)_2} + \mathrm{H_2}$$
$$4\mathrm{Fe(HCO_3)_2} + 2\mathrm{H_2O} + \mathrm{O_2} = 4\mathrm{Fe(OH)_3} + 8\mathrm{CO_2}.$$

Dunstan, Jowett, and Goulding[5] have suggested that the presence of carbon dioxide is not essential, but that the iron acts on the water and oxygen with formation of ferrous oxide and hydrogen peroxide. These two substances then interact with formation of hydrated ferric oxide:

$$\mathrm{Fe} + \mathrm{O_2} + \mathrm{H_2O} = \mathrm{FeO} + \mathrm{H_2O_2}$$
$$2\mathrm{FeO} + \mathrm{H_2O_2} = \mathrm{Fe_2O_2(OH)_2},$$

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[1] Smits and Lobry de Bruyn, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, 18, 807.

[2] Dunstan, Jowett, and Goulding, *Journ. Chem. Soc.*, 1905, 87, 1548; *Proc. Chem. Soc.*, 1907, 23, 63.

[3] *Mem. Manch. Phil. Soc.*, 1876, 5, 104.

[4] *J. Iron Steel Inst.*, 1888, ii., 129.

[5] *Loc. cit.*

the excess of hydrogen peroxide immediately reacting with iron to form a further quantity of rust. No evidence of the intermediate formation of hydrogen peroxide has been found, the authors basing their conclusion mainly on the fact that substances which destroy hydrogen peroxide appear also to prevent rusting.

Water is itself dissociated into $H^{\cdot}$ and OH' ions, and Whitney[1] has suggested that iron combines directly with the OH' ions to form ferrous hydroxide while hydrogen is liberated. The function of the oxygen is to oxidise the ferrous hydroxide to rust and also the hydrogen, thus disturbing the equilibrium and allowing the reaction to proceed further.

Whether pure oxygen and water in the complete absence of carbon dioxide or other acid will cause iron to rust has been the subject of much discussion. The researches of Moody[2] showed that under such conditions no rusting occurred. In his experiments, however, the iron was cleaned by means of chromic acid, and the criticism has been made that it was thereby rendered passive. Lambert and Thomson[3] found that an exceptionally pure sample of iron made by the reduction of carefully purified ferric nitrate did not rust, and it is therefore probable that the non-rusting of Moody's iron can be accounted for by the thorough cleaning of the metal. Lambert[4] consequently concludes that only an impure iron will rust, and that rusting is due to differences of solution tension of different parts of a heterogeneous surface of impure metal. The process is an electrolytic one and the oxygen acts as a depolariser by oxidising the hydrogen.[5]

The formation of rust takes place to begin with but slowly, but as soon as a thin, superficial layer of rust has been formed the process goes on rapidly. There is a difference of potential between rust and metal, so that electrolytic action is further increased.[6] Friend[7] has suggested that rusting itself is due to the catalytic action of a sol of a higher oxide of iron which oxidises the iron and is thus reduced, but is oxidised again by oxygen. He has shown that iron does not rust as quickly in moving water which would remove the sol, and that those substances which precipitate, dehydrate, dissolve, or act as protective colloids to the sol, also decrease rusting.

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[1] *J. Amer. Chem. Soc.*, 1903, **25**, 394.

[2] *Journ. Chem. Soc.*, 1906, **89**, 720; *Proc. Chem. Soc.*, 1907, **23**, 84.

[3] *Journ. Chem. Soc.*, 1910, **97**, 2426.

[4] *Ibid.*, 1912, **101**, 2056; *ibid.*, 1915, **107**, 218; *Proc. Chem. Soc.*, 1912, **28**, 197; *Trans. Faraday Soc.*, 1913, **9**, 108.

[5] See also Aitchison, *J. Iron Steel Inst.*, 1916, **I**, 77; Goudriaan, *Chem. Weekblad*, 1919, **16**, [40], 1270.

[6] See Aston, *Trans. Amer. Elect. Soc.*, 1916, **29**, 449.

[7] *Journ. Chem. Soc.*, 1921, **119**, 932; see also *Koll. Zeit.*, 1921, **28**, 207.

Certain salts, especially those of ammonia,[1] promote rusting, while alkalis and alkali carbonates inhibit it.[2]

Steel instruments may be kept bright by immersion in a solution of caustic soda, or, better, of sodium nitrate. In order to lessen the liability to rust, iron articles are coated with varnish or oil-paints, or the surface is covered with oil, grease, or graphite. A coating of magnetic oxide of iron, Fe_3O_4, is, however, the most efficient protection, and to obtain such a coating articles of iron are subjected to the action of superheated steam at a temperature of about 650°, this process being known, from the name of its inventor, as the Barff process.

In contact with zinc, iron becomes electronegative, and is thereby to a considerable extent prevented from rusting. Iron articles are therefore often covered with a coating of zinc to protect them from atmospheric corrosion. This is usually done by immersing the cleaned iron article in a bath of molten zinc (galvanising) or by packing the iron round with zinc dust in a closed chamber and heating to just below the melting point of zinc (sherardising). The former method is more extensively employed, but the latter gives a more resistant product.[3] Iron is also coated with tin by immersion in the molten metal (tin-plate) but in this case the protection lasts only as long as the layer of tin is intact. Once a portion of the iron becomes exposed it rusts much more rapidly than if no tin were present, because iron is electropositive in contact with tin. The coating of iron with nickel by electro-plating is another important method of protecting it from atmospheric action.

By alloying chromium with steel, a product is obtained which is capable of resisting all ordinary corrosive agents. It is put on the market as *rustless* or *stainless steel.*

533 *Iron amalgam* does not form readily, but on acting with a 1 per cent. sodium amalgam upon a solution of ferrous sulphate a semi-solid mass is obtained which, when in small globules, is attracted by the magnet. On distilling this amalgam, metallic iron remains in a state of fine division

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[1] See Vaubel, *Chem. Zeit.*, 1913, **37**, 693.

[2] See Friend and Marshall, *Journ. Chem. Soc.*, 1914, **105**, 2776; *Proc. Chem. Soc.*, 1914, **30**, 263.

[3] Halla, *Zeit. Elektrochem.*, 1913, **19**, 221.

(Böttger). The same amalgam can be formed by rubbing powdered iron with mercuric chloride and water. If an iron wire be attached to the copper pole of a Daniell element, and dipped into a solution of ferrous sulphate, whilst another iron wire from the zinc pole touches a drop of mercury lying in the solution, amalgams of varying composition are obtained according to the intensity of the current.[1] Those containing only small quantities of iron are liquid; those in which more iron is present are soft and crystalline. One containing 103·2 of iron to 100 of mercury forms a hard, black mass, and is obtained by submitting the liquid amalgam to a pressure of 50 tons to the square inch.

METALLURGY OF IRON.[2]

534 Several mythical stories point to the fact that in very early times meteoric iron, which, falling from the heavens, was considered as a gift of the gods to man, was employed in the manufacture of iron weapons. Kumbary[3] relates that the chiefs in the Wadai country, in Central Africa, possess many weapons which have been worked up from meteoric masses. But meteoric iron occurs so sparingly upon the earth's surface, and is, in fact, so unsuited to the manufacture of tough forgings, that at a comparatively early period in the history of civilisation men set about the smelting of iron from its ores.[4]

The enormous deposits of ancient slag and furnace-cinder which are found spread over large areas in various districts of India point to the fact that the iron industry existed in that country in very early times, and even to the present day the manufacture of iron is carried on in India in the most primitive manner. It is also clear that the ancient Assyrians and Egyptians were well acquainted with the uses of iron, and the remains of their iron works have been found near Sinai. But, independently of these sources, a knowledge of the methods of working iron ores also appears to have been gained by the tribes living in the North of Europe, whilst the inhabitants of the Western Hemisphere were not acquainted with these processes. Little is known respecting the method employed by the ancients in the manufacture of iron; the slight information which we possess has been collected together by Agricola in his works, "De Veteribus et Novis Metallis," and "De Re Metallica."[1] The apparatus employed was evidently of a primitive kind, and consisted of a small hearth or furnace to which was attached a bellows or blowing arrangement driven by hand, similar indeed to that which is now in use among the hill-tribes in India and in Central Africa. Malleable iron and steel are both produced by igniting the iron ore with charcoal, the metal being obtained in the form of a porous lump or "bloom," which is pressed or hammered into a coherent metallic mass.

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[1] Joule, *Journ. Chem. Soc.*, 1863, **16**, 378.

[2] Further information on this subject may be obtained from the metallurgical works of Percy, Turner, Howe, Harbord, Sexton, and Carnegie.

[3] *Compt. rend.*, 1870, **70**, 649.

[4] See "The Early Use of Iron," Brough, *J. Iron Steel Inst.*, 1906, **69**, 233.

The dexterity exhibited by the Hindus in the manufacture of wrought iron may be estimated from the fact of the existence near the Kutab Minar, Delhi, of a wrought iron pillar 24 feet in length.[2] This pillar stands about 22 feet out of the ground, and has an ornamental cap bearing an inscription in Sanskrit belonging to the fourth century. An analysis of specimens obtained from the actual pillar by Hadfield shows that the material is an excellent type of wrought iron, made with a very pure fuel, probably charcoal.

535 *Varieties of Iron and Steel.*—Iron which is obtained from its ores by metallurgical processes is never pure, but contains other constituents, which greatly affect the properties of the metal and determine its value for various purposes. The most mportant of these constituents are carbon, silicon, phosphorus, sulphur, and manganese, and, in special cases, nickel, chromium, tungsten, vanadium, cobalt, and molybdenum. It is found that comparatively small variations in the amount of these substances exert an enormous influence on the properties of the metal.

Four main varieties of commercial iron are usually distinguished:

(1) *Cast iron* contains 2·2–4·5 per cent. of carbon, besides varying quantities of the other elements mentioned above. This variety fuses readily, and when cold is brittle and cannot be worked under the hammer.

(2) *Wrought* or *malleable iron* contains little carbon and

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[1] See the translation from the Latin edition of 1556, by H. C. Hoover and L. H. Hoover; published by *The Mining Magazine*, 1912.

[2] A cast of this pillar was formerly to be seen in the Architectural Court of the South Kensington Museum, but was destroyed during a fire in 1885. A drawing of the pillar is found in St. John Day's *Prehistoric Use of Iron and Steel*, p. 144, and a reproduction from a photograph in the *J. Iron Steel Inst.*, 1912, 85, 168, Plate 14.

fuses with difficulty, but is malleable and can therefore be worked under the hammer, and can be welded at a red heat. The characteristic feature of malleable iron is that it is produced in a pasty state without having been melted, and consequently contains particles of slag, which cannot be completely removed from the unfused metal.

(3) *Steel* comprises all malleable alloys of carbon and iron which have at any time been actually melted. It contains very little slag, but otherwise does not necessarily differ in composition from malleable iron. Steel possesses the valuable property of becoming hard when it is suddenly cooled from a high temperature, the intensity of this effect depending largely upon the amount of carbon which it contains.

(4) *Special steels* contain, besides carbon, varying quantities of one or more of the following elements: manganese, nickel, chromium, tungsten, silicon, vanadium, molybdenum, and cobalt. Some of these steels have valuable mechanical and physical properties not possessed by ordinary carbon steels.

The general process of iron smelting consists essentially in the removal of the oxygen from the ores, and this is invariably carried out in practice by the action of carbon at a high temperature. In addition to the oxygen, the extraneous matter contained in the ore, such as silica, alumina, lime, sulphur, etc., must also be removed, and the resulting iron must be exposed to such conditions that it acquires the composition which will fit it for the special purpose to which it is to be applied.

536 *Ores of Iron.*—The term iron ore includes only those minerals which contain iron both in sufficient quantity and also in a condition which enables them to be employed for the economic production of the metal. Thus, for example, iron pyrites, FeS_2, which occurs in very large quantities and contains a high percentage of iron, cannot properly be described as an iron ore, although it is used as a source of iron after the removal of sulphur for the manufacture of sulphuric acid. In like manner, arsenical pyrites, although it also contains a large quantity of iron, is unfit for the production of the metal; and the same may be said of many other minerals which contain large quantities of iron.

The various ores of iron are composed of, or yield, the oxides of iron in more or less pure condition, and the value of an iron ore is influenced by the nature of the impurities which it contains as well as by the percentage of iron.

The ores of iron occur in almost every geological formation; thus magnetic iron ore is found in the older rocks, as in the Laurentian beds of North America, and the old slates and gneisses of Sweden, whilst red hæmatite occurs in beds or pockets in the carboniferous limestone of Cumberland and North Lancashire, and spathic ore and clay iron stone in the coal measures. Again, the oolitic rocks furnish large deposits of brown hæmatite, and the Elba ore is probably a tertiary deposit. Still more recent formations of iron ore are seen in the bog ore of Germany and the North of Ireland, whilst "lake ores" are being formed in Scandinavia at the present day. Analyses of various ores are given on page 1227.

Magnetic Iron Ore, Magnetite, or *Loadstone,* Fe_3O_4.—This ore, in the pure state, constitutes the richest ore of iron, containing 72·4 per cent. of the metal. It occurs in the crystalline and massive state as well as in the form of sand, and is found in large deposits, especially in volcanic rocks, as well as in granite, gneiss, and mica-schist. The most important localities of magnetite are Arendal, Dannemora, and other places in Norway, Sweden, and Lapland; the island of Elba; the Ural Mountains; and several localities in the United States, especially near Lake Superior. In England, magnetic oxide of iron occurs on Dartmoor, at Brent in South Devon, and at Treskerby in Cornwall; but it cannot be said to be an important English ore. In Germany it is found in large quantities at Schmiedeberg, in Silesia, and a few other localities.

Franklinite, $(Fe,Mn)_2O_3,(Fe,Zn)O$, occurs in New Jersey, and is first worked for zinc, the residue being used as an iron ore for the production of spiegeleisen.[1]

Red Hæmatite, or *Specular Iron Ore,* Fe_2O_3.—This substance occurs crystalline as specular iron ore, and also in a massive state having a columnar, granular, or botryoidal form, as well as in the earthy condition. Hæmatite occurs in veins as well as in beds and pockets. One of its most remarkable localities is the island of Elba, where it occurs finely crystallised between talcous schist and crystalline limestone. The Elba mines were worked by the Etruscans, and are still productive. A fine hæmatite occurs in the Huronian rocks on the southern shore of Lake Superior, whilst at Iron Mountain, near St. Louis, Missouri, enormous masses of this ore of iron are found. On the continent of Europe hæmatite occurs in Belgium, and deposits of this ore are found also in the Devonian formation on the Lahn in Westphalia. The chief deposits of hæmatite in England are those near Ulverston in Lancashire, and on the coast of Cumberland near Whitehaven; the ore here occurs in beds or pockets in the carboniferous limestone, sometimes existing as hard botryoidal masses exhibiting crystalline structure, and sometimes in a soft or compact amorphous condition.

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[1] *J. Iron Steel Inst.,* 1894, **45**, 416.

Brown Hæmatite, or *Limonite*, $Fe_2O_3,2Fe(OH)_3 = 2Fe_2O_3,3H_2O$. —This substance occurs crystallised in rhombic prisms, but is more frequently found either in a fibrous, foliated, and scaly condition, or as a dark brown, reniform mass and commonly known as Brown and Yellow Hæmatite. In the massive state this ore occurs in large quantity, and, as it can be readily worked, it has been long employed as a source of iron. It is found in the carboniferous limestone as well as in the older rocks, in the Forest of Dean, and at Llantrissant in Glamorganshire in the lower coal measure sandstones. At Bilbao, in Spain, it occurs largely in the carboniferous limestone, whilst the newer and earthy brown hæmatite is found in the oolite and greensand in Northamptonshire and Lincolnshire. It is likewise largely worked in Germany and France, being the ore from which the greater part of the iron made in these countries is derived. The bog ores which are worked in the plains of North Germany and Canada and in other places, as well as the peculiar iron ore of the North of Ireland and the Swedish lake ore, belong to this class, and are of the most recent geological formation.

Spathic Iron Ore, or *Siderite*.—Spathic iron ore consists of ferrous carbonate, $FeCO_3$, invariably mixed with the isomorphous carbonates of manganese, magnesium, and calcium. It possesses a yellowish-brown colour, and occurs often in globular or botryoidal forms having a silky, fibrous structure. It is usually found in Devonian rocks, occurring in England at Weardale in Yorkshire, at Brendon Hill in Somerset, and on Exmoor.

Clay Iron-stone, or *Argillaceous Iron Ore*, is a spathic iron containing clay, and is chiefly found in nodules or bands interspersed throughout the clays and shales of the coal measures. It is the most important English ore of iron. The chief workable British beds occur in Yorkshire, Derbyshire, Staffordshire, Warwickshire, South Wales, and Scotland.

The "black band" iron-stone is an important variety of this ore. It contains from 20 to 25 per cent. of carbonaceous matter, and is found in Lanarkshire, North Staffordshire, and South

Wales. The Scottish beds were discovered by Mushet in 1800, but they were not worked until the year 1830. In 1855 the same ore was discovered in Westphalia, and it is worked also in Lower Silesia. The coal measures of the Gard and of the Aveyron in France, and those in Pennsylvania and Maryland and other States, also contain large quantities of clay iron-stone. The same ore is found in strata in the lias and also in the oolitic and tertiary rocks, the Cleveland iron ore belonging to this last class.

537 *Preparation of Ores for Smelting.*—In many cases iron ores require no preliminary treatment before smelting other than breaking to a size suitable for the furnace. The correct size will depend on the nature of the ore. In most cases it is not profitable to concentrate the ore or to separate it from associated impurities before smelting, but in the case of certain magnetites, magnetic separators are used which concentrate the ore and at the same time considerably reduce the amount of phosphorus which occurs as non-magnetic apatite. The concentrates, which have necessarily been crushed to a fine state, are afterwards briquetted in suitable presses and hardened by submitting to a high temperature. In some cases a binder is introduced before briquetting, the most common being lime, the briquettes in this case being submitted to the action of high pressure steam for hardening.

Many methods of sintering, agglomerating or nodulising fine ores such as the residues of pyrites burners have been recently introduced, some of which are carried out in a similar manner to that used in the blast roasting of galena (p. 906).

The carbonate ores, clay iron-stones and brown hæmatites are submitted to a process of calcination prior to smelting. Calcination is carried out in kilns, and during the process water is expelled, carbonic acid driven off, sulphur reduced considerably, coaly matter burnt, and ferrous oxide converted into ferric oxide. The operation also results in a more porous material suitable for reduction by the agency of carbon monoxide in the furnace.

THE MANUFACTURE OF IRON.[1]

538 The application of the blast furnace to the manufacture of iron marks an era in the history of the iron industry, inasmuch as it was by its use that a continuous process of iron manufacture

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[1] For further information on this subject the reader is referred to Percy's admirable "Sketch of the History of Iron," *Iron and Steel*, p. 873, and to Turner's *Metallurgy of Iron*, 1 *et seq.*

Analyses of the Chief Ores of Iron.

	Magnetic Iron Ore.	Red Hæmatite.	Brown Hæmatite.		Spathic Iron Ore.	Clay Iron-stone.	
	Sweden.	Ulverston.	Forest of Dean.	Spain.	Erzberg.	Lowmoor.	Cleveland.
Ferrous oxide	28·42	—	—	—	55·64	36·14	39·92
Ferric oxide	62·06	86·50	90·05	78·80	—	1·45	3·60
Manganous oxide	—	0·21	0·08	0·65	2·80	1·38	0·95
Alumina	—	—	trace	3·50	—	6·74	7·86
Lime	—	2·77	0·06	trace	0·92	2·70	7·44
Magnesia	1·44	1·46	0·20	trace	1·77	2·17	3·82
Alkalis	—	—	—	—	—	0·65	0·27
Carbonic acid	—	2·96	—	—	38·35	26·57	22·85
Sulphur trioxide	—	0·11	trace	—	—	—	—
Iron sulphide	0·07	—	—	—	—	0·10	0·11
Phosphoric oxide	—	trace	0·09	0·07	—	0·34	1·86
Silica	7·60	6·55	1·07	5·55	—	17·37	7·12
Insoluble matter					—	—	—
Water	—	—	9·22	11·65	—	1·77	2·97
Organic matter	—	—	—	—	—	2·40	1·64
Total	99·59	100·56	100·77	100·22	99·48	99·78	100·41

became possible. The discovery of a process by which fusible iron can be prepared appears to have been made, probably accidentally, about the end of the fifteenth century, in Germany, where the Stückofen had long been in use for manufacturing blooms. No description of the process is, however, to be found in the older writers upon metallurgy. Thus Agricola, writing in 1556, mentions only the older methods of iron making, although he appears to have been acquainted with cast iron; at any rate, the new method must have been at work in this country in 1543, for we find that in that year English cast iron cannons were used. The great demand for cast iron, which was all made with charcoal, soon leading to a destruction of our forests, it became necessary, in the first year of the reign of Elizabeth, to endeavour to replace charcoal by some other fuel. This was accomplished by the employment of coke instead of charcoal, a practice which was carried out in England by Dudley as early as the first half of the seventeenth century, but which afterwards fell into abeyance. It was subsequently revived by Abraham Darby at Colebrookdale, about 1735.

The blast furnace consists of a shaft varying in height from 50 to 100 feet, the largest diameter being 14 to 24 feet. The essential parts of the furnace are, first, the hearth or crucible, and, second, a shaft or chimney formed of two truncated cones joined at their bases, the upper being termed the "body" and the lower one the "boshes." Fig. 189 shows the construction of such a furnace on the scale of 1 : 180.

The shaft, A, Fig. 192, is 75 feet high, the diameter at the widest part (the belly or bosh) being 20 feet, whilst at the throat, B, it is 16 feet, and at the hearth, C, 11 feet. The shaft is constructed of an outer shell of wrought iron or mild steel plates, supported by means of cast iron columns, D, and is lined with fire-brick. In the lining of the boshes, which is exposed to the highest temperature, cooling boxes are inserted. These consist of narrow, flat boxes made of bronze, which are built into the brickwork, and are cooled by a current of water, thus preventing the brickwork from becoming too hot. The wall of the hearth, which is also lined with fire-brick, is pierced by several openings; the tapping hole, E, by means of which the molten iron is periodically withdrawn; the slag-notch (not shown in the diagram), which is situated at a higher level, and through which the lighter slag is allowed to flow away into trucks or ladles; and, finally, the openings by which the blast of air is introduced through the tuyères.

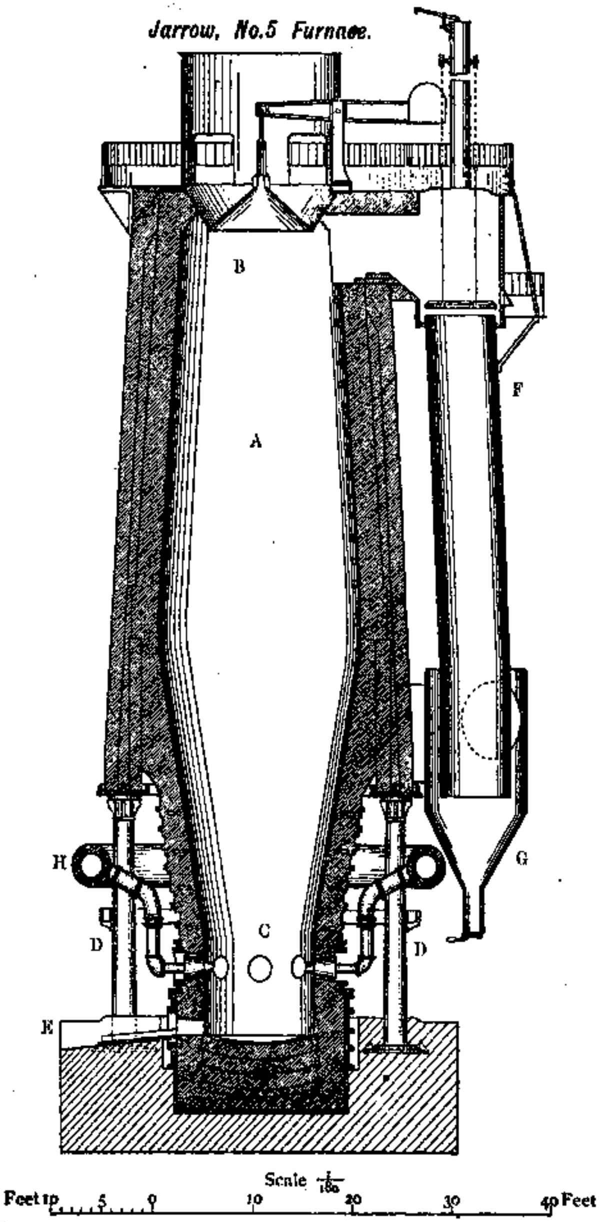
Jarrow, No.5 Furnace.
B
A
F
H
G
C
D
D
E
Scale $\frac{1}{180}$
Feet 10 5 0 10 20 30 40 Feet

Fig. 192.

The throat of the furnace is closed by a contrivance known as the cup and cone arrangement, first introduced by G. Parry at the Ebbw Vale works in 1850. It consists of a cast iron funnel, fixed at the mouth of the furnace, and closed by a cast iron cone, suspended at one end of a counterpoised lever, or by means of a chain and wheel. The charge is tipped from barrows on to the cone, and is introduced into the furnace by momentarily lowering the latter. When the cone is raised against the funnel (as shown in the figure) the throat of the furnace is closed, and the escape of gases into the air prevented; these then pass out of the furnace by the downcast, F, which is provided with a dust-catcher, G, and are, after further cleaning, conveyed through the main to the stoves for heating the blast, to the boilers, or to any other point where the heat produced by their combustion can be made available. The gases are also frequently used direct in gas engines.[1]

The blast of air is introduced near the bottom of the furnace through tuyère holes, perforating the walls of the hearth. The tuyères are made of wrought iron, cast iron, or bronze, and have a double casing through which water circulates to keep them cool; they vary in number from 8 to 16, according to the size of the furnace, are about 5 to 7 inches in diameter, and are fed from an annular pipe, H, which surrounds the lower part of the furnace, and is connected with the blowing engine.

Hot and Cold Blast.—Up to the year 1828 air was blown into the furnace at the ordinary atmospheric temperature, but in that year J. B. Neilson[2] patented a process for heating the air before it passed into the furnace, and this process, inasmuch as it saved from 15 to 25 per cent. of the fuel, and was also accompanied by an increased productive power of the furnace, was soon generally adopted, although the cold blast is still employed in some works for the manufacture of certain brands of cold blast iron. For the purpose of heating the air, the waste gases from the furnace are burned in a Cowper's or Whitwell's stove or some modification of these, such as the Massick and Crookes, the Ford and Moncur, or the Cowper-Kennedy; all these act on the principle of the Siemens regenerator, and after being heated sufficiently the gas supply is diverted and cold air passed through on its way to the furnace. The air is thus introduced at a temperature of about 700° to 800°, and at a pressure of about 5 lb. to the square inch.

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[1] Hubert, Reinhardt, and Westgarth on Blast-furnace Gas Engines, *J. Iron Steel Inst.*, 1906, **71**, 16—169.

[2] Patent No. 5701, March 3rd, 1828.

The total capacity of a furnace such as that described is about 14,150 cubic feet, and it is capable of producing about 1,000 to 1,300 tons of iron per week.

Dry Air Blast.—An important development in blast furnace practice is the drying of the air before passing it through the stoves.[1] This is accomplished by drawing the air through refrigerators in which the moisture is removed. By this means it is possible under certain climatic conditions to increase the burden and production of pig-iron by 20 per cent., to reduce the amount of coke per ton of iron by 18 per cent., and to diminish the duty on the blowing engines on account of the colder air being denser. The greatest advantage is, however, in the regularity of working the furnace, because the amount of moisture carried into the furnace by the blast varies very largely from day to day with change of atmospheric conditions, so that the burden of the furnace must have a safe margin of fuel to allow of a sudden loss of heat due to this cause.

539 *The Working of the Furnace.*—For the purpose of starting the newly-built blast furnace it is necessary that the whole should be gently heated by means of a fire, usually made by piling a quantity of rough dry timber in the hearth, on to the top of which charges of coke are placed. As soon as the shaft has become warm, regular charges of calcined iron-stone, limestone, and coke are added, until the furnace is filled. The blast is then turned on to about one-fifth of the quantity usually employed, the size of the tuyères being gradually increased until the furnace is in full work.

The proportion of the materials employed, viz., iron ore, limestone, and fuel, termed the *charge* or *burden*, varies considerably according to the nature of the ore. If it be siliceous or clayey, additions of lime must be made; whilst if the ore contain lime instead of silica, the addition of silica may be required. The object of these additions is to form fusible slags, so that the gangue of the ore may be removed and the furnace kept open and in proper working. The slag consists of calcium and aluminium silicates, and it is extremely important that it be kept of the right basicity and fusibility. If the supply of lime and alumina be insufficient to combine with the silica present, oxide of iron passes into the slag, thus causing waste, whilst if an excess of these bases be used the lining of the furnace is attacked. The fusibility of the slag, moreover, determines the temperature which can be reached, and is therefore of great importance, as this has a great effect on the nature of the iron produced. The higher the temperature which is required for the reduction of the ore the less fusible must be the slag. As soon as the proper proportions between the fuel, ore, and limestone have been ascertained, it is of the greatest importance that these proportions should be strictly adhered to, and for this purpose the charges are regularly weighed or measured and supplied at the top of the furnace, into which they are charged by lowering the cone as already described.

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[1] Gayley, *J. Iron Steel Inst.*, 1904, 66, 274; 1905, 67, 256. See also Daubiné and Roy, *J. Iron Steel Inst.*, 1911, 83, 23.

On the average about one ton of coke and 8 to 12 cwt. of limestone are required for each ton of iron produced, about 5 tons of heated air being used in the operation. When the furnace is in regular blast, a constant stream of slag passes out from the slag-hole, the iron collecting in the lower part of the hearth, and being from time to time tapped by piercing a plug of sand and clay by which the tap-hole has been closed. Before tapping, moulds are prepared for holding the metal; these are formed in the sand as a series of parallel trenches, which are placed in communication with the tap-hole. The blast of air is then shut off, and the tap-hole opened by piercing the plug with a long bar of iron. The molten iron flows into the channels communicating with the moulds and assumes the form of semi-cylindrical bars or " pigs " united to one another by one of larger dimensions termed the "sow."

If, owing to some accident to the machinery, a blast furnace is obliged to stand when hot, the operations may be suspended for several months if the throat and tuyère-holes are closed up with sand or clay. Should, however, serious damage have occurred, the furnace must be "blown out." This is accomplished by reducing the burden, and thus increasing the temperature for a time so as to remove any aggregations of solid matter which are fusible only at a high temperature. Finally only fuel is charged, the contents of the furnace are allowed to burn out, and the last tapping is made at a point as low down in the hearth as possible. The life of a blast furnace varies considerably, lasting from five to twelve years, or even for a longer time, according to circumstances.

The size and shape of blast furnaces have been and continue to be very different. When charcoal is employed, as was formerly universally the case, and is still so in countries where wood is plentiful, the furnace is usually only from 20 to 30 feet in height. The charcoal iron which is thus manufactured in Sweden, Russia, and America is especially valuable for the preparation of crucible steel. Blast furnaces in which the fuel used is either coke, anthracite, or splint coal, are, on the other hand, of much larger dimensions, the exact height and capacity of the furnace being regulated by the nature and amount of iron which has to be produced, as well as by the nature of the ore and fuel to be used.

In the year 1750 each English blast furnace produced about 300 tons of pig-iron per annum, whereas a large-size modern furnace yields up to 70,000 tons in the same period. In the Cleveland district, where the blast furnaces are usually large, the average capacity of those built up to the year 1854 was about 7,000 cubic feet; whilst those built during the years 1870 and 1871 have an average capacity close upon 30,000 cubic feet; in some cases, however, the height rises to 105 feet, and the capacity to 50,000 cubic feet. The production of a blast furnace increases, of course, with its size, but not in a direct ratio; thus Lowthian Bell has shown that an old furnace of 1853, having a capacity of 6,000 cubic feet, yielded one ton of iron per twenty-four hours for every 190 cubic feet of space; whilst in the high furnace built in 1870, 380 cubic feet of space are required to produce one ton of iron in the same time; hence the maximum limit of economic action may be passed by increased size.

The maximum production is at present gained in America, where furnaces 75 to 90 feet in height are employed, and the blast is fed at a higher pressure, averaging about 10 lb. to the square inch. The furnace thus works more rapidly, producing as much as 100,000 to 150,000 tons per annum.[1]

540 *Chemical Changes in the Furnace.*—A large number of investigations have been made on the subject of the changes which occur in the blast furnace, but in spite of these our knowledge of them is still far from complete. The fuel at the hearth, uniting with the oxygen of the blast, which is insufficient for its complete combustion, burns with formation of carbon monoxide. This gas, coming into contact with the constantly descending

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[1] One of the Carnegie Steel Company's furnaces produced 918 tons of pig-iron in twenty-four hours on March 30th, 1905.

charges of ore, reduces the ferric oxide to spongy metal, the change being accompanied by a slight evolution of heat:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 + 8,652 \text{ cal.}$$

The zone in which this reduction occurs most rapidly is near the top of the furnace, its exact position depending on the nature of the ore, and its temperature varies from 600–900°. When the ores are porous they are more easily permeated by the carbon monoxide, and the reduction takes place more quickly than when denser ores are employed. The reduction in this upper zone is never quite complete, because metallic iron is itself oxidised when heated either in carbon dioxide or in carbon monoxide, free carbon being deposited in the latter case. As the spongy iron, still containing a small amount of oxide, descends, it arrives at the hotter parts of the furnace, the temperature of which reaches 1000° in the belly or widest section. At this point the reduction of the metal is completed by the solid carbon present, some of which is supplied by the dissociation of carbon monoxide, which takes place at a high temperature, with formation of carbon dioxide and free carbon.[1]

Below this zone is the hottest part of the furnace, and the materials, which were formerly in a pasty state, melt completely, running down into the hearth, where the lighter slag floats on the surface of the heavier iron, and thus protects it from the oxidising action of the blast. Other important changes in the composition of the iron occur as the metal passes down the furnace. In the first place, the spongy iron, in passing through the zone of reduction, takes up sulphur from the ores and fuel; and secondly, when the temperature reaches the highest point in the zone of carburisation, the phosphates contained in the ore are reduced, and the phosphorus is taken up by the iron. At a still higher temperature the fused iron in the presence of carbon reduces the silicates to silicon; this, with manganese and other metals, remains as a constituent of the iron.

It will thus be seen that three main zones may be distinguished in the furnace. In the *first* and highest, the greater part of the reduction occurs, whilst the partially reduced mass, in passing through the *second*, acquires the high temperature which is necessary for the reactions occurring in the *third* and last zone. These comprise the complete reduction of the ore, the carburisation and fusion of the metal, and its impregnation with silicon, phosphorus, etc. These various zones are, of course, not well defined, but pass gradually one into the other.

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[1] Cailletet, *Compt. rend.*, 1866, **62**, 891.

541 *Gases of the Blast Furnace.*—The composition of the blast furnace gases naturally varies in the different zones and under different conditions of burden. The relation of the carbon dioxide to carbon monoxide present in the blast furnace gases is of great interest. The monoxide is reconverted during the reaction into the dioxide, and this either remains unaltered or is reconverted by the iron into the monoxide, according to the temperature which prevails in the upper part of the furnace. Carbon dioxide also is formed near the top of the furnace by the calcination of the limestone, and this is then partly reduced to the monoxide. The researches of Lowthian Bell and von Tunner have shown that the relation between the volumes of the escaping carbon dioxide and carbon monoxide, under otherwise similar conditions, serves as an excellent criterion of the economical working of the blast furnace, and the limit of economical working is reached when from 40 to 60 volumes of carbon dioxide are present for 100 volumes of carbon monoxide. The furnace gases contain, in addition, nitrogen of the air, hydrogen from the reduction of aqueous vapour, hydrocarbons, and, frequently, traces of cyanogen or hydrogen cyanide.

Many analyses of the blast furnace gases, collected at various heights above the tuyères and in varying circumstances, have been made. The following figures give an idea of the varying nature of the composition of these gases:

Wood Charcoal Furnace at Veckerhagen, near Cassel. Height, 5·97 m. (Bunsen).

Depth in metres below the mouth—	0·86	2·59	4·32
Nitrogen	62·34	63·89	64·58
Carbon dioxide	8·77	3·60	5·97
Carbon monoxide	24·20	29·27	26·51
Methane	3·36	1·07	1·88
Hydrogen	1·33	2·17	1·06
	100·00	100·00	100·00

Hot-blast Coke Furnace at Seraing in Belgium. Height, 14·43 m. (Ebelmen).

Depth in metres below the mouth—	0·30	3·05	13·71
Nitrogen	57·06	61·67	54·63
Carbon dioxide	11·39	1·08	—
Carbon monoxide	28·61	35·20	45·05
Methane	0·20	0·33	0·07
Hydrogen	2·74	1·72	0·25
	100·00	100·00	100·00

Cold-blast Coal Furnace at Alfreton. Height 11 m. (Bunsen and Playfair).

Depth in metres below the mouth—	1·52	5·18	10·36
Nitrogen	55·35	55·49	58·05
Carbon dioxide	7·77	12·43	—
Carbon monoxide	25·97	18·77	37·43
Methane	3·75	4·31	—
Hydrogen	6·73	7·62	3·18
Ethylene	0·43	1·38	—
Cyanogen	—	—	1·34
	100·00	100·00	100·00

When coal is employed in the blast furnace instead of coke, the waste gases are passed through coolers and scrubbers to remove the valuable tar and ammonia which they contain, and are then passed on to the Cowper stoves, etc.

During the war of 1914–1918, considerable quantities of potash salts were recovered from the waste gases and flue dust of blast furnaces and additions of common salt were made t the charge in order to displace the potash contained in th materials.

An interesting substance sometimes found in the blast furnac is a cyano-nitride of titanium (p. 847); and, in addition to this, "kish," or graphite, as well as silicates and the oxides of othe metals, occur as solid deposits in the furnace.

The slags produced during the smelting of iron ores in blast furnaces vary considerably in appearance, properties, and composition, and are produced by the combination of the gangue and flux. The colour and appearance of the slag afford a valuable indication of the working of the furnace. With an excess of lime, as is used in the manufacture of open-grained grey iron, the slag is difficultly fusible, and when solid is white and of low specific gravity. For a finer grained grey iron, a less basic slag is required, and this is harder, more compact, and usually of a grey colour with a tinge of blue or green. With a white iron, the slag produced is dark in colour and has a higher specific gravity. The chemical composition of the slags varies widely with different mixtures, and consists chiefly of silica, lime, and alumina. The following analyses are given to indicate the wide differences which may be found in slags from different sources: slag A was obtained from a furnace making grey iron, and slag B from a furnace making white iron:

	A	B
Silica	29·81	42·23
Alumina	19·94	9·84
Lime	40·31	37·13
Magnesia	2·95	1·32
Manganous oxide	trace	0·97
Ferrous oxide	trace	2·60
Calcium sulphide	6·92	4·32

VARIETIES OF CAST IRON.

542 Molten iron usually contains 2·2–4·5 per cent. of carbon, and when the iron is cooled this is either entirely, or only partly, retained in combination by the metal, whilst the remainder separates out in the form of graphite, its behaviour being determined by the composition of the mass, the conditions of the process of manufacture, and the mode of cooling. When the greater part of the carbon separates in the form of graphite, the resulting metal is known as *grey iron*, whilst when the whole or the greater part of it is retained in combination by the iron the metal is known as *white iron*. Between these are several intermediate conditions classed together as *mottled iron*. All these names are derived from the appearance of a freshly fractured surface of the metal, the mottling characteristic of the last class being caused by the occurrence of spots of grey in a matrix of white iron.

When white iron is dissolved in hydrochloric or sulphuric acid, various hydrocarbons are formed at the expense of the combined carbon which it contains, and these impart a peculiar and disagreeable odour to the hydrogen which is evolved. On the other hand, when grey iron is treated with acids the graphite separates out in the form of black, insoluble scales. This fact was known to Bergman, whilst Guyton de Morveau proved that cast iron is formed when wrought iron is ignited with diamond powder; and Karsten showed that cast iron contains carbon both in the combined state and free in the form of graphite, this latter remaining behind when the iron is dissolved in an acid. The graphite can also be mechanically separated from the iron by sieving (Snelus).

Both the total amount of carbon present and the mode in which it occurs depend very largely on the other substances contained in the crude iron, whilst these, of course, are determined by the conditions of the manufacture. Thus chromium and manganese favour the presence of a large amount of carbon, which is retained in combination when the iron cools, whereas silicon diminishes both the total amount of carbon present and the proportion of it which remains in the combined form. The way in which the metal is cooled also has a very important influence on the mode of occurrence of the carbon, slow cooling promoting the crystallisation of graphite and the consequent production of grey iron, whilst sudden cooling or chilling favours the production of the more homogeneous white iron. It is therefore possible, within certain limits, to obtain either grey or white iron from a given mass of the fused metal, simply by altering the conditions of cooling.

The following analyses of Cleveland pig[1] show the gradual variation in composition from grey through mottled to white iron:

	Grey.	Mottled.	White.
Carbon, Graphitic . . .	3·20	1·84	—
„ Combined . .	trace	1·25	3·05
Silicon	3·50	1·01	0·67
Sulphur	0·05	0·32	0·40
Phosphorus	1·76	1·57	1·60
Manganese	0·68	0·62	0·42

White Iron is formed when the furnace is working on a heavy burden or at a comparatively low temperature. It is very hard and brittle, and when fractured presents a very close grain. It melts at a lower temperature than grey iron, is less liquid, and after cooling is often found to be vesicular or honeycombed from the evolution of gas given off as the metal cools.

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[1] Quoted by Turner, *Metallurgy of Iron*, 3rd ed., p. 280.

Grey Iron, on the other hand, is produced at a higher temperature, has an open-grained fracture, melts to a thinner liquid, and is better adapted for fine castings than white iron.

Mottled Iron is intermediate in its properties between white and grey iron.

Spiegel or *Specular Iron* is a variety of white iron in which manganese is present as an essential constituent, and contains a large proportion of carbon, varying from 3·5–6 per cent., practically all of which is in the combined form. It is extremely hard and brittle, and has a specific gravity of 7·6–7·7. When the alloy contains more than about 25 per cent. of manganese it attains a granular structure and is termed *ferromanganese*, which commonly contains 80 per cent. of manganese. These two materials are largely used in the manufacture of steel by the Bessemer and open hearth processes as deoxidisers and recarburisers.

Some analyses of pig-irons are given on p. 1241.

In foundry practice, castings of grey iron are made by pouring the molten metal into suitably prepared sand or loam moulds. The molten iron is obtained in the foundry by melting a mixture of several grades of pig-iron together with a quantity of foundry and other scrap in a cupola or small blast furnace, using coke as a fuel, and with the addition of a little limestone to flux off the ash of the coke and the silica adhering to the pig-iron used. The castings thus produced are always somewhat brittle, and in the manufacture of malleable iron castings, which are much less brittle, the castings are first produced in white iron and then packed in iron ore and submitted to a long annealing process, during which the combined carbon is converted into finely graphitic or temper carbon and is also partially removed by oxidation from the surface.

MANUFACTURE OF WROUGHT OR MALLEABLE IRON.

543 Malleable iron can be produced, either by the direct reduction of the ore in such circumstances that it cannot take up sufficient carbon, etc., to convert it into cast iron, or

indirectly from cast iron by the removal of carbon and some of the other constituents.

(I.) THE DIRECT REDUCTION OF MALLEABLE IRON FROM THE ORES.

544 *Iron Furnaces.*—The simplest form of the iron furnace is that used on the west coast of India, as well as in the Deccan and Carnatic, and amongst the hill-tribes. The low-caste Hindus who work in iron wander from place to place and build up their simple apparatus where they find fuel and ore, this latter consisting generally of magnetic oxide or brown hæmatite. The furnaces are built on the ground and constructed in the form of a small round shaft or chimney. At the lower part there are two openings, one of which serves for the blast and the other for the exit of the slag as well as for the extraction of the bloom of iron. The bellows are usually made from a goat's skin or a buffalo hide, furnished with bamboo tubes. As soon as the furnace is warmed with charcoal, layers of the broken ore and charcoal are put in the shaft, and after from 4 to 6 hours a porous bloom of iron is obtained, varying in weight from 5 to 30 lb., and this is then worked under the hammer. Throughout Central India and in the north-east provinces the manufacture of iron is somewhat further advanced, the furnaces being larger and of a similar character to those which have been or are still in use in various parts of the world, as in Africa, Borneo, and certain parts of Europe. In many localities in England furnaces were erected on high ground, so as to take advantage of the prevailing wind to increase the draught. The word "hammer," which frequently occurs in place-names in the south of England, usually marks the location of one of these old smelting works with its accompanying forge.

(II.) PRODUCTION OF MALLEABLE IRON FROM PIG-IRON.

545 The change which occurs in the conversion of pig-iron into malleable iron consists essentially in the removal of a large proportion of the carbon, silicon, sulphur, phosphorus, and manganese from the former, and is effected by oxidation in the presence of some substance which can unite and form a fusible slag with the silica and phosphoric oxide produced. As the removal of carbon, etc., proceeds, the melting point of

Analyses of Pig-irons.

		Graphite.	Combined Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Chromium.	Iron.	Tungsten.
White	Durham	—	4·10	0·23	0·03	0·07	2·37			
„	Alabama	0·10	2·92	0·95	0·30	0·64	0·10			
„	South Wales	—	2·40	0·80	0·70	1·50	0·20			
„	Staffordshire	0·20	2·00	0·71	0·19	0·47	0·50			
„	Schwechat	—	2·83	0·52	0·08	0·18	2·67			
Mottled	Ilsenburg	3·77	0·53	0·43	0·15	trace	1·43			
„	Cleveland	2·28	0·72	1·35	0·03	1·17	—			
„	Forest of Dean	2·37	1·31	0·40	0·06	0·07	0·11			
Grey	Forest of Dean	3·90	0·39	1·07	0·01	0·07	0·22			
„	Scotland	4·40	trace	2·68	0·08	0·10	—			
„	Staffordshire	3·30	0·40	1·88	0·02	0·71	0·40			
Spiegel	Dannemora	—	4·81	0·18	trace	0·12	1·99	—	92·90	
Spiegel	Siegen	—	5·04	0·41	0·08	—	5·75	—	88·56	
Ferromanganese	Prieger	—	7·15	0·87	0·02	0·07	72·75	—	19·14	
Ferrosilicon	Darwen	1·20	0·23	14·00	0·08	0·08	1·95	—	—	
Ferrochrome	Darwen	—	10·05	0·40	—	—	0·42	63·10	25·38	
Ferrotungsten	—	—	2·87	0·85	0·10	0·05	0·47	—	43·20	51·74

the iron rises, so that at a certain stage the metal begins to solidify. It is then worked into a porous ball or bloom, and hammered in order forcibly to squeeze out the slag which is contained in the pores.

The Puddling Process.—In 1784 Henry Cort introduced the puddling process, the essential feature of which is the use of a reverberatory furnace instead of an open-hearth furnace formerly used for the oxidation of the constituents of the cast iron. In the older form of the process the oxidation was effected chiefly by the oxygen of the air. The process was applicable only to white iron, and thence necessitated a preliminary *refining* of the metal when grey iron was employed. The metal was charged along with a sufficient quantity of coke into an open hearth furnace, and there melted and exposed to the blast from six tuyères. When the oxidation had proceeded far enough to reduce the percentage of silicon to the requisite point, the tap-hole was opened, the iron allowed to run into moulds, and the cast iron cooled by water. The refined iron is highly crystalline, white, and brittle, the carbon being present in the combined state. The following analyses by Abel of pig-iron, before and after refining, from Königshütte in Silesia, give the different percentages of silicon, phosphorus, and sulphur, and show that in this process the silicon is largely eliminated, whilst sulphur and phosphorus are less affected; the total amount of carbon, moreover, is not much altered.

	Pig-iron.	Refined Iron.
Silicon	4·66	0·62
Phosphorus	0·56	0·52
Sulphur	0·04	0·03

The slag obtained in this process, known as *refinery-slag*, forms, when cold, a dark, crystalline mass, with an almost metallic lustre. It consists chiefly of ferrous silicate, Fe_2SiO_4, in which, however, a part of the iron may be replaced by manganese, calcium, magnesium, etc. Not infrequently, distinct crystals of olivine, $(Mg,Fe)_2SiO_4$, have been found.

The refined iron was then melted on the bed of a reverberatory furnace and stirred by means of iron instruments, so as to expose it thoroughly to the air. As soon as the oxidation had been carried out to a sufficient extent, the metal was removed and treated as already described.

The Modern Puddling Process.—In England and other countries where grey pig is largely made, the preliminary process of refining has been done away with, and the pig-iron is at once submitted to the operation of puddling without previous refining, the process being termed "pig-boiling."

An ordinary puddling furnace is shown in elevation, section, and plan, in Figs. 193, 194, 195. The bed or hearth of the furnace (*h*) is supported by a cast iron plate; at each end of the hearth, which is usually 6 feet long, is a wall built of fire-brick, one end being called the fire-bridge (*b*), and the other the flue-bridge (*d*). The bottom and side plates of the hearth are lined with a coating of tap-cinder, which is heated until it becomes soft, and is then spread evenly over the floor of the hearth. Above this is placed a coating or "fettling" of ferric oxide of about 1½ inches in thickness, and this is renewed from time to time as it wears away. Neither of these coatings is shown in the figures. The fire-bars, which are sometimes placed in a slanting position, are seen at *r*, and the area of the grate should be from one-half to one-third of that of the bed. A powerful draught is obtained by means of a brick chimney, the top of which is furnished with a damper, which can be opened and shut at will by the workman by means of a handle, and thus the passage of air through the furnace regulated. In some furnaces gas is employed with a Siemens regenerator; oil and natural gas have also been used as a source of heat.

The distinguishing feature of the modern process consists in the fact that the iron is fused in contact with the oxides of iron which are present in the fettling, and with a fusible slag which is added to each charge. In this way the oxidation of the carbon, etc., is carried out mainly at the expense of the oxygen of the fettling, and since an equivalent amount of metallic iron is thus produced the loss is rendered much smaller. The time required for the oxidation is also greatly lessened, the whole operation lasting only two hours. As soon as the charge has been completely melted, it is well stirred, so that it is thoroughly exposed to the action of the fettling and of the air. It is then allowed to cool somewhat, and well mixed, whilst in a pasty state, with the oxide of iron present. This brings about the oxidation of the carbon with formation of carbon monoxide, probably thus:

$$Fe_2O_3 + 3C = 2Fe + 3CO,$$

and the escape of this gas causes the whole mass to swell up or

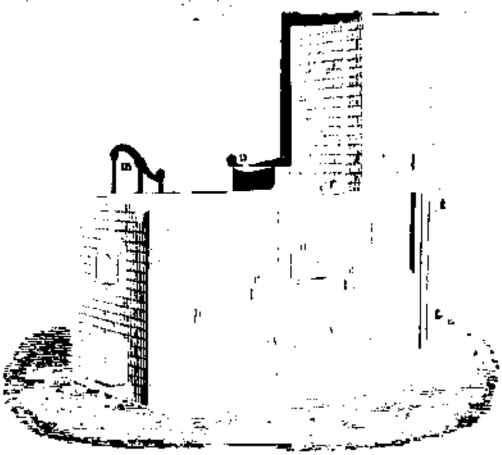

Fig. 193.

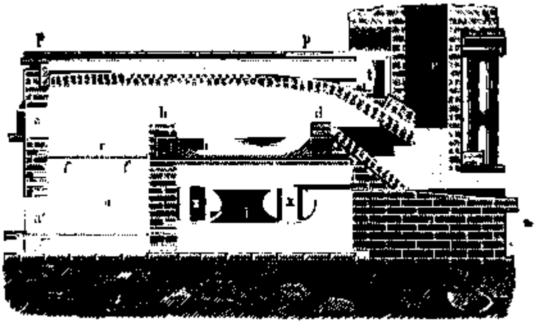

Fig. 194.

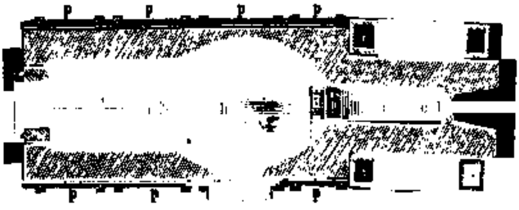

Fig. 195.

"boil." The iron then gradually subsides a little into a porous mass, or as it is termed, "comes to nature," and is worked into balls which are removed from the furnace and hammered to get rid of the fusible slag and to weld the porous iron into a homogeneous mass, this process being completed by passing the metal through the rolling mill. It is to this treatment that the characteristic fibrous structure of the wrought iron is due.

Mechanical Puddling Process.—In order to avoid the heavy manual labour necessary in the ordinary puddling processes, revolving puddling furnaces have been invented by Danks, Roe,[1] and others. These furnaces are in use to a small extent, but have not been generally adopted.

546 The following analyses made by J. G. Snelus give an idea of the consecutive chemical changes which take place in the passage from cast to wrought iron: (*a*) is the mottled Cleveland iron which was puddled in the Danks revolving furnace; (*b*) a portion taken out when melted; the composition ten minutes later is shown by (*c*); after a lapse of twenty minutes by analyiss (*d*); the composition of the bloom is shown in (*e*); and of the puddled bar in (*f*); C.C. stands for combined carbon, and G.C. for graphite:

	Fe.	C.C.	G.C.	Si.	P.	S.	Mn.
a . .	93·19	1·45	1·38	1·24	1·49	0·11	0·63
b . .	95·03	2·83	—	0·82	0·91	0·09	—
c . .	96·46	2·80	—	0·20	0·58	—	—
d . .	98·09	1·17	—	0·05	0·52	—	—
e . .	98·40	0·15	—	0·09	0·45	—	—
f . .	97·13	0·15	—	0·14	0·47	0·04	0·14

It will thus be seen that the silicon is first burned out along with most of the phosphorus, whilst the carbon afterwards disappears.

A large proportion of the phosphorus contained in the pig is found in the slag or *tap-cinder* as phosphide and phosphate; the sulphur is left in the cinder as iron sulphide. The tap-cinder is rich in iron, and is employed, after roasting in heaps, as fettling, or for the manufacture of common iron. The following analyses of tap-cinder give an idea of its composition:

SiO_2.	FeO.	MnO.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	P_2O_5.	S.	Analyst.
7·71	66·32	1·29	8·27	1·63	3·91	0·34	8·07	1·78	Riley.
11·76	58·67	0·57	17·00	2·34	2·88	0·29	4·27	3·11	"
29·60	48·43	1·13	17·11	1·28	0·47	0·35	1·34	1·61	Percy.

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[1] *J. Iron Steel Inst.*, 1906, 71, 264.

547 *Properties of Malleable Iron.*—Good hammered and rolled bar-iron, when it contains from 0·1 to 0·25 per cent. of carbon, possesses a fibrous texture, but when the amount rises to 0·5 or above it possesses a granular or crystalline structure. Fibrous iron is soft and possesses a grey colour; granular iron is harder and has a dead silvery lustre. The hardness of iron increases with the amount of carbon. Malleable iron melts at from 1,500° to 1,400°,[1] according to the amount of carbon which it contains. The physical properties of commercial malleable iron vary widely, being largely influenced by the nature and amount of the impurities which the iron contains; thus, for instance, sulphur imparts to iron the property of becoming brittle when hot, or, as it is technically termed, "red-short," whilst phosphorus renders iron weak at the ordinary temperature, when the iron is said to be "cold-short." Cold-short iron exhibits a peculiar fracture, and the property of cold-shortness apparently depends upon a peculiar crystalline condition of the iron.

Malleable iron of good quality should have a minimum tensile strength of 22 to 25 tons per square inch with the grain, and 18 to 20 tons per square inch across the grain; it should show an elongation of 18 to 25 per cent. on eight inches, and should bend double without fracture.

(III.) THE MANUFACTURE OF STEEL.

548 Steel was obtained in early times directly from the ore in a similar manner to that used for the manufacture of malleable iron. The Chalybes on the coast of the Black Sea were renowned for their ability in working the iron ores into steel, and the Greek name for steel, χάλυψ, appears to have been derived from the name of this tribe.

The older chemists looked upon steel as a peculiarly pure form of iron, and "Basil Valentine," in his *Last Testament*, terms it the "hardest, purest, most malleable iron." Lemery held peculiar views respecting steel. In his *Cours de Chymie*, published in 1675, he says: "Le fer est un métal fort poreaux, composé de sel vitriolique, de soufre et de terre mal lié et digéré ensemble. On le réduit en acier par le moyen des cornes ou des ongles d'animaux, avec lesquelles on le stratifie et ensuite on le calcine; ces matières contenant beaucoup de sel volatile qui est alcali, tuent les acides de fer qui tenoient ses pores ouverts, et le rendent plus compacte."

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[1] Carpenter and Keeling, *J. Iron Steel Inst.*, 1904, 65, 232.

Stahl considered iron to be an impure metal containing earthy materials, whilst steel was the pure metal saturated with phlogiston. Similar views were held by the later chemists. Bergman was the first to distinguish chemically between wrought iron, steel, and cast iron. He found that the first when dissolved in acids yielded the largest quantity of inflammable air, steel somewhat less, whilst cast iron gave the smallest quantity; hence he concluded that steel contained less phlogiston than wrought iron. He also showed that cast iron contained more graphite than steel, and this more than wrought iron, and hence he concluded that cast iron was converted into steel by loss of graphite and by absorption of phlogiston, whilst he supposed that when steel was produced from wrought iron the opposite reactions occurred. Rinmann in 1782 developed similar views, and he especially insisted that malleable iron was a perfect metal, and was converted into steel by absorption of phlogiston, but that this phlogiston was not the substance usually thus designated, but plumbago. In 1786 Monge, Vandermonde, and Berthollet published a research proving that the difference between the various kinds of iron is determined mainly by the variation in the amount of carbon which they contain, but the many doubtful points which remained were cleared up only by the comprehensive researches of Karsten and Sefström.[1]

As already explained (p. 1223), the amount of carbon present has now been found not to provide a convenient distinction between malleable iron and steel, since specimens of these may contain the same amount of carbon and yet possess very different properties, owing to different internal structures.

Steel can be made in a very large number of different ways, the principles of which may be roughly summarised thus:

A. Directly from the ore.
B. From malleable iron.
  1. By the direct addition of carbon, accompanied or followed by fusion.
  2. By fusion accompanied by the addition of more highly carburised metal.
C. From pig-iron.
  1. By the removal of carbon and other impurities.
  2. By the addition of a less highly carburised metal, such as malleable iron.

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[1] Percy, *Iron and Steel*, p. 116.

Many of the processes actually adopted involve two or more of these methods, and the number of different processes now employed is very large, but only two or three of the most important and typical methods are here described.

549 *The Cementation Process.*—Seventy years ago the only method by which steel could be made was the decarburisation of the cast iron in the puddling furnace, and the subsequent recarburisation of the puddled bar by the cementation process. The product was then either fused in a crucible, yielding cast steel, or drawn out under the hammer, whereby tilt steel or shear steel was obtained.

The cementation method of preparing cast steel is mentioned by Agricola in his *De Re Metallica*, whilst that for hammered or tilt steel was first described by Réaumur in 1722.

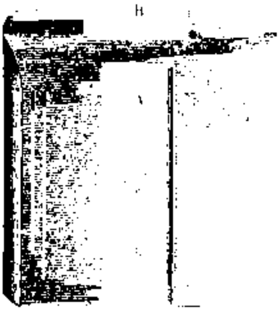

Fig. 196.

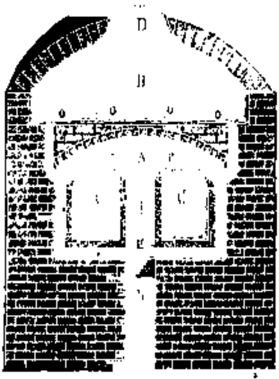

Fig. 197.

In the manufacture of steel by the cementation process carbon is added to the otherwise pure wrought iron. This is carried on in the furnace shown in Figs. 196 and 197. Into the furnace are built two square boxes or "converting pots," c, c, Fig. 197, of infusible fire-brick; and in these are placed the bars of iron which are to be converted into steel. The flames from a fire placed in the hearth (*g*) play round these boxes. The iron which has to be converted into steel is usually in the form of straight bars about 3 inches broad, and 0·75 inch thick, which are somewhat shorter than the converting pot in which they are placed. The interstices between the bars when piled in the pot are filled up with powdered charcoal, technically termed "cementing powder," a thick layer of the charcoal being placed on the top of the bars, and the whole mass plastered over with grinders' waste. The total weight of iron contained in each box is from five to six tons. The fire is gradually raised to a full red heat, 1000–1100°, and is maintained at this point for about seven to ten days, according to the quality of steel which is needed. Spring steel requires seven days, shear steel eight days, and steel for welding from nine to ten days. During the operation trial bars are removed by the openings (*c*) from the ends of the chests, and when it is found that the bar-iron has been completely converted into steel the furnace is allowed to cool, and after several days the charge is removed. The steel bars thus obtained retain the form of the original iron, but in physical properties they differ considerably from the original. Thus the coloured surface of the fractured bar of steel has no longer the bluish tint of malleable iron, but has acquired a reddish tint, not very different from that of bismuth, and the texture has become distinctly crystalline. The steel is also much more fusible than malleable iron, a varying amount of carbon having been taken up.

The following is an analysis by David Forbes of cementation steel made at Sheffield from Swedish iron :

Combined Carbon.	Graphitic Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
0·627	0·102	0·030	0·005	0·000	0·120.

A remarkable alteration of the surface is likewise noticed in the passage of wrought iron into steel, it being covered with blisters, and hence it is termed *blister steel*. The formation of these blisters is undoubtedly due to the production of gas within the bar, the gas resulting from the combination of a part of the carbon with oxygen derived from the particles of oxide of iron contained in the slag in the interior of the bar. The bars are finally cut up, sorted according to their quality as indicated by the fracture, melted in crucibles, and finally cast in ingots.

Various hypotheses have been proposed to account for the phenomena observed in the cementation process. According to one view, the carbon is absorbed from the exterior and passes to the interior of the bar partly from the solid carbon, partly from the carbon monoxide formed by its partial combustion, and partly from the hydrocarbons derived from the hydrogen contained in the charcoal. The probability of the view that the carbon monoxide is the active agent is strengthened by the fact observed by Graham, that red-hot iron has the power of absorbing from eight to ten times its volume of this gas.

It also appears probable that the carburisation of the iron may be due in part, if not altogether, to the formation of carbide of iron (Fe_3C) and to an actual diffusion of this into the bars. This phenomenon would then be analogous to the inter-diffusion of metals in the solid state which has been described by Roberts-Austen (p. 95).

550 *Crucible Steel.*—The cast steel made by melting cemented bars in a crucible is of excellent quality, and is employed for the best classes of cutlery. Many other qualities of steel may also be obtained by the use of crucibles as already indicated; iron of various qualities being melted with carburising materials, or with iron of a different carbon content.

In other cases malleable iron is melted with charcoal, or with cast iron. In all cases the molten metal cannot be immediately poured into the ingot mould, as the castings produced would then be full of vesicles. It is therefore allowed to remain in tranquil fusion for some time before pouring, or ferro-aluminium is added, and the metal at once poured. The castings are then found to be sound and free from vesicles.

551 *Bessemer Steel Process.*—Since the year 1856 a complete revolution has taken place in the iron industry, and this has been caused mainly by the discovery of a method for manufacturing cast steel, on the large scale, from cast iron. This discovery was made by Bessemer,[1] and first communicated in a paper read before the Mechanics Section of the British Association, at its Cheltenham meeting, in 1856, and entitled "The Manufacture of Malleable Iron and Steel Without Fuel." The process consists in removing the carbon, silicon, and manganese contained in pig-iron by oxidising them by means of a blast of air blown through the molten metal, the heat evolved by the oxidation being sufficient to keep the whole in a liquid state until the pig-iron is converted into steel, which is thus effected without the intermediate laborious and costly processes of puddling and cementation. The first experiments which were made were unsuccessful, for although by this process the carbon and silicon can be removed, the phosphorus and sulphur which are contained in the pig remain in the finished steel, and for this reason the ordinary impure English pig-iron yielded unsatisfactory results. The case, however, was otherwise when

[1] Brit. Patent, Dec. 7, 1855, No. 2768.

the pure Swedish charcoal-pig was used; indeed, the first real success in working the process was achieved with this iron at the Högbo Ironworks, at Sanviken, and this was followed by the successful use of grey iron made from the Ulverston hæmatite, and now technically known as *Bessemer-pig*. Other difficulties then arose such as the too complete oxidation, when the whole of the carbon is burnt out, a mass of pasty wrought iron being produced instead of liquid steel. This was overcome by the important suggestion made by Mushet[1] of the addition of spiegel at the end of the operation in such quantity as is necessary for the conversion of the whole of the wrought iron into steel.

The oxidation is carried on in an egg-shaped vessel, termed the converter (Figs. 198–9), made of wrought iron plates bolted firmly together and lined with an infusible siliceous rock termed ganister, which is ground, moistened with water, and applied to the interior. The lower portion is an interchangeable bottom, consisting of a shallow lower section of the vessel with tuyère-box or wind-box and tuyères, together with the necessary arrangements for fixing these in their places. This bottom is attached to the vessel in such a manner that the narrow space between it and the vessel lining may be rammed with plastic ganister by men working outside the vessel, and this joint can be easily made at once upon pulling away the old bottom. This arrangement is of great advantage, inasmuch as by its use the number of blows per diem can be considerably increased. The pig-iron, which must be free from phosphorus and sulphur, is first melted in a cupola, and from five to twelve tons of this are run into the converter, either directly from the cupola or from an intermediate ladle, the mouth of the converter being lowered to the proper angle to receive the molten metal. The converter is then gradually raised to the vertical position; at the same time a moderate blast of air is forced through the tuyères by means of the pipes L, N̄, and D, the pressure of the blast being afterwards raised to from eighteen to twenty pounds per square inch.

The combustion of the silicon, manganese, and carbon, as also of a portion of the iron, then begins, and the temperature rises to a point sufficiently high to keep the metal liquid. In the first part of the blow the graphite is converted into combined carbon, and a highly siliceous slag is formed, a portion of the silica being derived from the lining. When the first period is complete, an orange-yellow flame edged with blue appears at the mouth of

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[1] Brit. Patent, Sept. 22, 1856.

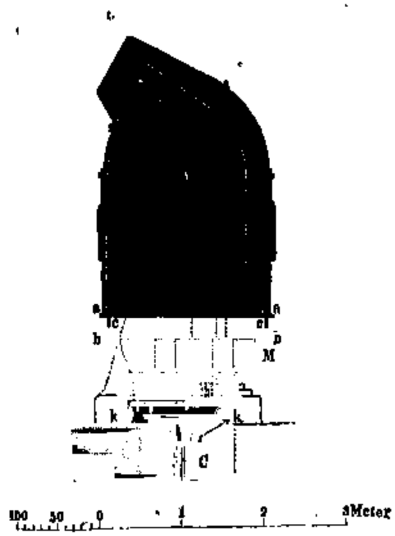

FIG. 198.

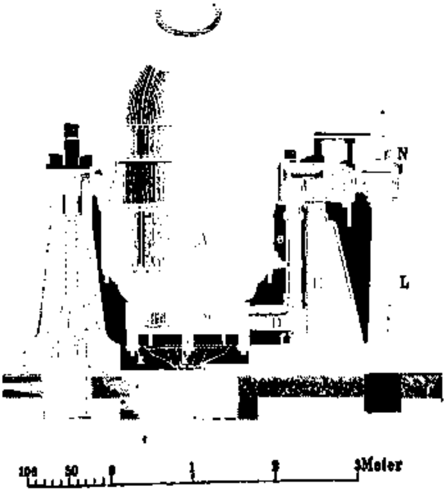

FIG. 199.

the converter, and the second period, termed the "boil," then begins. In this, the slag containing oxide of iron oxidises the carbon, with formation of carbon monoxide which escapes throughout the mass, giving to it the appearance of a boiling liquid. During this period particles of the slag and molten iron are thrown out from the mouth of the converter, and a very brightly luminous, flickering flame makes its appearance, accompanied by a rapid stream of sparks due to the combustion of the particles of iron. After the lapse of from six to eight minutes the intensity of the action diminishes, the shower of sparks ceases, and suddenly the flame disappears and is said to drop. The whole of the carbon has now been oxidised, and, if the blast be left on, the combustion is continued at the expense of a portion of the iron. Hence, the force of the blast is now lessened, the converter inclined, then the blast stopped, and the requisite amount of spiegel or ferromanganese introduced to bring the steel to the requisite degree of carburisation. The blast is then turned on again for a few seconds, or the mixture is simply allowed to stand for a short time, and the whole mass poured out into the ladle. After standing for a few minutes in the ladle, the fluid steel is cast into ingot moulds, and the cast steel worked up under the hammer and in the rolling mill. The whole process lasts from twenty to thirty minutes, and in this time from five to twelve tons of iron are converted into steel.

552 The chemical changes which the pig iron undergoes in the various stages of the Bessemer process, as well as the composition of the slags obtained, are tabulated below.

(*a*) Composition of the pig-iron used (3,517 kilos.). (*b*) After the first period of twenty-eight minutes' blow. (*c*) After the second period of seven minutes' blow. (*d*) After the third period of three minutes' blow. (*e*) Finished steel (3,058 kilos.) after the addition of 168 kilos. of spiegel.

Composition of Bessemer Metal.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	3·180	—	—	—	—
Combined carbon	0·750	2·465	0·909	0·087	0·234
Silicon	1·960	0·443	0·112	0·028	0·033
Phosphorus	0·040	0·040	0·045	0·045	0·044
Sulphur	0·018	trace	trace	trace	trace
Manganese	3·460	1·645	0·429	0·113	0·139
Copper	0·085	0·091	0·095	0·120	0·105
Iron	90·507	95·316	98·370	99·607	99·445

Composition of Bessemer Slag.

	a.	b.	c.	d.	e.
Silica	40·95	46·78	51·75	46·75	47·25
Alumina	8·70	4·65	2·98	2·80	3·45
Ferrous oxide . .	0·60	6·78	5·50	16·86	15·43
Manganous oxide .	2·18	37·00	37·90	32·23	31·89
Lime	30·36	2·98	1·76	1·19	1·23
Magnesia	16·32	1·53	0·45	0·52	0·61
Potash	0·18	trace	trace	trace	trace
Soda	0·14	trace	trace	trace	trace
Sulphur	0·34	0·04	trace	trace	trace
Phosphorus . . .	0·01	0·03	0·02	0·01	0·01

Converter Gases.—Snelus has investigated the composition of the gases issuing from the converter. When the charge lasted eighteen minutes he found the following results on analysis of the gases drawn out at the times after the commencement of the blow given in minutes in the first horizontal line:

	2.	4.	6.	10.	12.	14.
CO_2 . . .	10·71	8·59	8·20	3·58	2·30	1·3
O . . .	0·92	—	—	—	—	—
CO . . .	—	3·95	4·62	19·59	29·30	31·11
H . . .	88·37	0·88	2·00	2·00	2·16	2·00
N . . .		86·58	85·28	74·83	66·24	65·55

Elimination of Phosphorus.—It was at first supposed that the non-elimination of phosphorus in the Bessemer process was due to the high temperature, and that if the process could be conducted at a lower temperature, as in puddling, all the phosphorus would be found in the slag. Messrs. Thomas and Gilchrist[1] and Snelus have, however, proved that it is possible to eliminate phosphorus completely in the Bessemer process by using a basic lining of calcined dolomite for the converter instead of the usual siliceous one, phosphate of lime and magnesia being produced. This is known as the "basic" process, and is now largely in use in the case of phosphoric pig; it constitutes one of the most important advances in metallurgy, since it renders possible the direct production of steel from ordinary pig-iron, such as Cleveland pig, which contains comparatively large quantities of phosphorus.

The process is carried out in the main like the ordinary Bessemer process, but differs from it in one or two points. A certain amount of lime is placed in the converter and heated by the combustion of a small quantity of coke before the molten pig is run in. The blow is then conducted in the ordinary way, but when the flame has dropped the blow is continued, and it is in this "after blow" that the phosphorus is chiefly removed. This is well shown in the following table, which gives the results of a "blow" by the basic process: (*a*) gives the composition of the Cleveland pig, (*b*) after five minutes' blow, (*c*) after ten minutes, (*d*) after fifteen minutes, (*e*) after eighteen minutes. As soon as the phosphorus has been removed, a point which is indicated by the appearance of the fracture of a small sample of the metal, the process is concluded in the usual way by the addition of spiegel or ferromanganese. The slag, which contains the whole of the phosphorus in the form of phosphate, is ground and sold as a valuable manure.

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[1] *J. Iron Steel Inst.*, 1879, 120.

	a.	*b.*	*c.*	*d.*	*e.*
Carbon	3·50	3·55	2·35	0·07	trace
Silicon	1·15	0·50	0·09	trace	0·00
Manganese . . .	0·71	0·56	0·27	0·12	trace
Phosphorus . . .	1·57	1·60	1·43	1·22	0·08
Sulphur	0·16	0·14	0·13	0·12	0·10

Application of the Spectroscope to the Examination of the Bessemer Flame.—It has already been stated that the point at which the flame drops is that at which it is found by practice to be necessary to stop the blast, but it is not always easy to hit this point with accuracy; and if the blow be stopped a few seconds too soon, or carried on for a few seconds too long the quality of the resulting steel suffers. The application of the spectroscope to the determination of this point was made by Roscoe in 1863,[1] and has since been investigated by Watts, Lielegg, Snelus, Hartley,[2] and others.

The spectroscope is more extensively used on the Continent than in this country for the examination of converter flames;[3] and in Belgian and Swedish foundries is used to control the blow in operations in which the whole of the carbon is not eliminated but the air blast is stopped while the metal still contains 0·4 to 0·6 per cent. of carbon. At the beginning of the blow the spectrum is continuous and indefinite. With the faint appearance of the flame the characteristic yellow line of sodium is seen, and for a short period this line is very faint and appears in flashes. As the flame and temperature rise, the spectrum lines become more complex, the line spectrum of thallium and lithium and the banded spectrum of many other metals may be observed, but they are not of any particular value for the control of the blow. The principal lines to be noted are those of carbon, which appear bright green. They are faint at first, but gradually as the flame rises they become brighter and more distinct, until, with the falling of the flame, they diminish in number and fade completely away with the final drop of the flame.

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[1] *Proc. Manch. Phil. Soc.*, 1862–3, **3**, 57.

[2] *J. Iron Steel Inst.*, 1895, **48**, 95; also 1901, **60**, 197.

Campbell. *The Engineer*, 1921, **122**, 137.

553 *Open-hearth Processes.*—In these methods a reverberatory furnace is used, such as that shown in section in Fig. 200, which represents a 12-ton Siemens regenerative steel furnace. The furnace works on the regenerative system exactly as described on page 596; CC′ and DD′ are the chambers used for absorbing the waste heat of the furnace and for heating the gas and air; *k* is the hearth of the furnace, made of infusible siliceous material in the acid process and of dolomite in the basic process, the latter being used when the pig-iron contains phosphorus.

In the simple Siemens process a charge of pig-iron, together with scrap iron or steel when available, is put on the hearth of the furnace and melted. When the charge is fused, iron ore in the form of hæmatite is added from time to time. A violent reaction takes place on the addition of the ore, slag first being formed by the oxidation of the silicon present to silica, which combines with ferrous oxide from the ore.

After the silicon has been oxidised and removed, the metal "comes to the boil," the carbon present being oxidised by the basic ferrous slag, carbon monoxide being evolved and a certain amount of iron liberated. The end of the process is determined by the quality of steel required, and is tested by taking out a small sample and judging by the fracture obtained.

When the process is finished, the metal is tapped and a small amount of ferromanganese added to deoxidise and recarburise it.

Instead of charging the furnace with pig-iron, liquid metal[1] is sometimes used direct from the blast furnaces or from large gas-fired containers or metal mixers, as this considerably shortens the time necessary to work off a charge.

In the basic open-hearth process, employed for making steel from phosphoric pig-irons, a certain amount of lime and limestone is charged in with the pig, ore, and scrap; further quantities

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[1] "The Use of Fluid Metal in the Open-hearth Furnace," Riley, *J. Iron Steel Inst.*, 1900, **57**, 22.

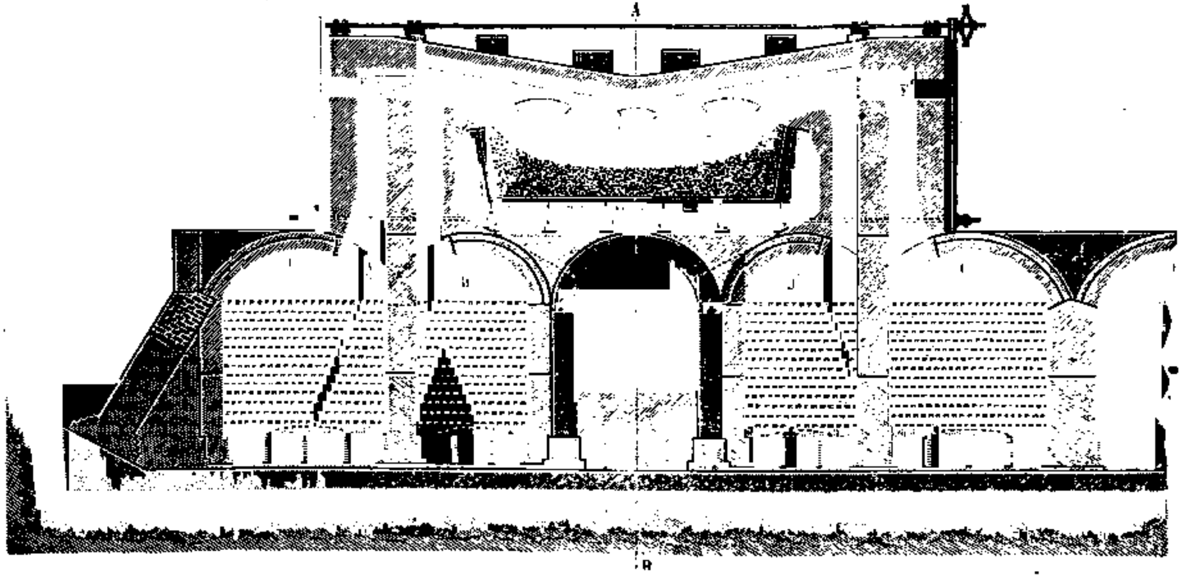

Fig. 200.

are added during the working, to keep the slag basic, the final slag containing from 40 to 50 per cent. of lime.

554 *Tilting Furnaces.*—Tilting furnaces[1] have been introduced to overcome the difficulties of tapping large charges from the furnaces. Of these the Wellman rolling-furnace is an example, in which the furnace is a strong steel shell lined with silica bricks. Underneath the body of the furnace are two curved rockers which roll on strong steel standards with horizontal surfaces. When pouring off slag or steel, the furnace is rocked forward by means of two hydraulic cylinders mounted on trunnions at their lower ends, and having the upper ends of their piston-rods attached to the pouring side.

Many modifications of the open-hearth process are now in use. Among these may be mentioned the Bertrand-Thiel[2] process, in which two or more furnaces are used to complete the operation. As generally practised, two open-hearth furnaces are used, preferably placed at different levels, so that the metal can easily be transferred from one to the other. Both furnaces are basic-lined. The pig is charged into the first furnace and is worked in the usual way; the scrap to be used is charged into the second furnace and is heated up and oxidised; the molten steel from the first furnace is then run into the second, where a vigorous reaction takes place, the non-metals being rapidly eliminated. By this process the time needed for working off a charge is considerably shortened and the yield materially increased, especially when large tilting furnaces and molten iron are used.

Another important modification is the Talbot process,[3] for which large basic-lined tilting furnaces are used, which have a capacity of 50 to 75 tons. The week's run is commenced on Sunday evening with a charge of pig and scrap, the charge being worked down to steel in the usual way with ore and lime. When this metal is of the required quality, about one-third of the charge is poured off, the furnace is turned back, and a considerable quantity of oxide of iron is added to the slag. When this is thoroughly melted, a charge of molten pig-iron is run in to replace the amount tapped out. A vigorous reaction at once takes place between the oxide of iron in the slag and the non-metals present in the iron, with a great elevation of temperature, so that during this reaction the gas-supply employed for heating the furnace is cut off. After the metal has "boiled" for ten or fifteen minutes, the slag is partly poured off and the bath finished off with additions of ore and lime. About one-third of the charge is again run off and the process is repeated as before, until the end of the week, when the furnace is emptied for repairs. The chief advantages claimed for this process are a saving in fuel, an increase in output and yield, and a saving in charges for labour and furnace repairs.

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[1] Head, *J. Iron Steel Inst.*, 1899, 55, 69.

[2] Bertrand, *ibid.*, 1897, 51, 115.

[3] "The Open-hearth Continuous Steel Process," Talbot, *J. Iron Steel Inst.*, 1900, 57, 33.

555 Electric furnaces are being used to a considerable extent in the production of high-class carbon and special steels from cold scrap, and also in the refining of steel from open-hearth furnaces and Bessemer converters in order to improve its quality. Three types of furnace are used: (1) The Induction Furnace, (2) The Resistance and Arc Resistance Furnace, and (3) The Arc Furnace.

556 The ordinary Bessemer ingots are frequently found to be honeycombed and unsound from the presence of blowholes, and the same thing is found in all large steel castings. These blowholes are small cavities or bubbles distributed throughout the metal, and vary in size from visible holes to microscopic cavities. Many suggestions have been made for the prevention of blowholes, and one process largely used consists in exposing the molten steel during its solidification to enormous pressure by means of hydraulic machinery.[1] Casting under pressure was first attempted by Bessemer in 1856, but was reintroduced and rendered practicable by Whitworth in 1865.

For the production of sound castings and the elimination of blowholes, silicon and aluminium are often added to the molten steel, the silicon as ferro-silicon and the aluminium as metal; very little aluminium is required for the purpose, and in the finished steel generally only a trace can be found.

557 *Properties of Steel.*—The most characteristic property of high carbon steel is its power of assuming an almost adamantine hardness when quickly cooled, as when plunged into water. After this treatment it is extremely brittle, almost perfectly elastic, and so hard that it cannot be attacked by a file. The hardness and brittleness may be practically removed by annealing, that is to say, heating the steel to a high temperature and then allowing it to cool slowly. It may also be partially removed

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[1] Capron, *J. Iron Steel Inst.*, 1906, 69, 28.

by a process of tempering which consists in heating the steel moderately and then allowing it to cool. The temper of steel depends upon the heat to which the steel is raised, and the workman judges as to the temperature by observing the various colours which the surface of the metal assumes during the progress o the operation. The tints thus observed are the colours of thin plates caused by the different thicknesses of the oxide formed on the surface. When the requisite tint is reached the object is quickly cooled by being plunged into water, brine, oil, etc. The hardest temper, such as is required for steel for surgical instruments, lancets, and razors, is that obtained at the lowest temperature; the tint employed for this purpose is that first reached and is a light-straw colour, the temperature being about 230° At 255°, a brownish-yellow tint is attained, and steel thus tempered is best fitted for cold chisels and shears for cutting metals. At 265°, the first shade of purple shows itself, and this is the temper employed for axes, plane-irons, and similar tools. A temperature of 277° gives a purple which is the tint for cutlery and cloth-shears, and for swords and watch-springs the metal is cooled when it has a bright blue colour, corresponding to a temperature of 288°. At higher temperatures, from 290° to 316°, steel assumes a dark blue colour, and is used for shears, chisels, and especially for large saws.[1]

Damascening is produced by repeatedly welding, drawing out and doubling up a bar composed of a mixture of steel and iron the surface of which is afterwards treated with an acid. The surface of the iron retains its metallic lustre under the action of the acid, whilst that of the steel is left with a black, firmly attached coating of carbon.

Case hardening is effected by more highly carburising the surface of mild steel. Objects of mild steel are heated together with nitrogenous organic matter such as powdered charcoal, bone-dust, leather, etc., or potassium ferrocyanide, and thus a superficial coating of more highly carburised steel is given to them.

The *Harvey process* is of a similar character, and is applied to armour plates in order to give them a hard surface capable of offering resistance to a modern projectile. This process is carried out by heating the plate of mild steel or nickel steel to about the melting point of cast iron in contact with carbonaceous material, which is tightly rammed down upon its surface. When the surface of the plate has absorbed about 1 per cent. of extra carbon the plate is withdrawn from the heating chamber and quenched with cold water.

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[1] See also *Report of the Lathe Tools Research Committee of the Manchester Association of Engineers*; published by the Department of Scientific and Industrial Research, 1922.

Manganese steel is very tough and is largely used for the jaws of rock breakers and other mining and mechanical machinery. Nickel is added to increase the tenacity and elastic limit, without reducing the ductility. Chromium increases the hardness, whilst tungsten and molybdenum prevent the softening effect of the rise of temperature of the tool.

The following tables give analyses (by Lambert) of various modern steels.

	Carbon.	Manganese.	Silicon.	Phosphorus.	Sulphur.	Copper.
Mild steel for structural work	0·247	0·476	0·063	0·052	0·049	0·054
Steel boiler plate	0·208	0·534	0·088	0·047	0·048	0·025
Steel rail, Indian Government	0·420	0·866	0·085	0·074	0·066	0·049
Steel tyre, N. B. Railway	0·534	0·902	0·248	0·045	0·054	0·038
Steel axle, British specification	0·320	0·756	0·186	0·038	0·035	0·051
Casting for hydraulic press	0·415	0·805	0·310	0·072	0·060	—
Casting for ship's stern frame	0·393	0·730	0·164	0·055	0·048	traces
Gun steel, British	0·385	0·648	0·182	0·038	0·035	0·029
Forged shaft for ship's propeller	0·345	0·555	0·098	0·040	0·042	0·055
Double shear steel	0·668	0·107	0·055	0·012	0·018	—
Spring steel, laminated, carriage	0·645	0·732	0·044	0·036	0·032	0·045
Tool steel for heavy work	0·750	0·468	0·238	0·021	0·018	0·022
Steel for swords, cutlasses, etc.	0·986	0·255	0·124	0·017	0·020	—
Die steel for striking coins	1·085	0·264	0·133	0·011	0·009	traces
Tool steel for light work	1·274	0·252	0·148	0·018	0·012	—
Cast steel for razors, surgical instruments, etc.	1·445	0·305	0·112	0·014	0·016	traces

	Carbon.	Manganese.	Silicon.	Phosphorus.	Sulphur.	Special Element.
Hadfield's manganese steel	0·875	13·330	0·068	0·030	0·047	—
Ordnance steel	0·330	0·606	0·165	0·029	0·038	Ni, 3·94
Chrome projectile steel	0·807	0·505	0·246	0·012	0·055	Cr, 5·74
Self-hardening tool steel	0·650	0·190	0·608	traces	0·042	W, 9·87
American self-hardening tool steel	0·585	traces	0·034	0·009	0·014	Mo, 9·16
High speed steel	0·612	0·288	0·214	0·012	0·019	W, 18·21 Cr, 3·85

558 *Recalescence of Steel.*—When ordinary steels, containing varying amounts of carbon, are allowed to cool from a temperature of about 1000°, it is found that at two or more temperatures

the regularity of the cooling is interrupted, an evolution of heat taking place which prolongs the period required for the metal to cool through a given range of temperature. This phenomenon is known as recalescence, and the temperatures at which the retardation during cooling takes place are indicated by Ar_3, Ar_2, and Ar_1; as these changes are reversible, there is a retardation of the rate of heating on raising the temperature of the steels, and the temperatures at which this retardation takes place are indicated by Ac_1, Ac_2, and Ac_3. These changes do not generally take place at the same temperature, the Ac point often being 30° higher than the corresponding Ar point.

The Ar_3 change[1] is found only in steels containing not more than 0·38 per cent. of carbon, and varies from 900° in pure iron to 770° in a steel of this composition; the Ar_2 change takes place at about 770°; and the Ar_1 change takes place at about 690°. These changes are not equally well marked in all varieties of steel. The Ar_1 change is the most pronounced and can sometimes be observed by the naked eye when cooling down large masses; it can also be rendered evident by allowing a heated bar of steel to cool when loaded with a weight just insufficient to bend it when hot. When the iron reaches the temperature of recalescence, it is seen suddenly to bend.

559 *Constitution of Steel.*—Many different views are held by chemists as to the constitution of steel, and the cause of hardening and of recalescence. All agree in regarding the Ar_1 change as due to the separation of carbide of iron, Fe_3C. All carbon steels which are slowly cooled from above this temperature (700°) contain the greater portion of the carbon in the form of this carbide, whilst steel which is suddenly cooled from a higher temperature contains scarcely any of it in the free state.

According to one view (the "Allotropic"),[2] the two changes Ar_2 and Ar_3 mark the occurrence of allotropic changes in the iron present; the metal being supposed capable of existing in three allotropic forms, as γ-iron above Ar_3, as β-iron between Ar_3 and Ar_2, and as α-iron below Ar_2; of these varieties, γ- and β-irons are non-magnetic (see p. 1217). When heated steel is suddenly cooled, the γ- or β-form persists and the result is a hard and brittle metal; if the temperature be allowed to fall below Ar_2, the α-form is produced, and a soft metal is the result. In the absence of carbon, the β-form invariably passes into about the melting point of cast iron in contact with carbonaceous material, which is tightly rammed down upon its surface. When the surface of the plate has absorbed about 1 per cent. of extra carbon the plate is withdrawn from the heating chamber and quenched with cold water.

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[1] Carpenter and Keeling, *J. Iron Steel Inst.*, 1904, **65**, 224.

[2] See Stansfield, *ibid.*, 1899, **56**, 169; 1900, **58**, 317.

Manganese steel is very tough and is largely used for the jaws of rock breakers and other mining and mechanical machinery. Nickel is added to increase the tenacity and elastic limit, without reducing the ductility. Chromium increases the hardness, whilst tungsten and molybdenum prevent the softening effect of the rise of temperature of the tool.

The following tables give analyses (by Lambert) of various modern steels.

	Carbon.	Manganese.	Silicon.	Phosphorus.	Sulphur.	Copper.
Mild steel for structural work .	0·247	0·476	0·063	0·052	0·049	0·054
Steel boiler plate	0·208	0·534	0·088	0·047	0·048	0·025
Steel rail, Indian Government .	0·420	0·866	0·085	0·074	0·066	0·049
Steel tyre, N. B. Railway . . .	0·534	0·902	0·248	0·045	0·054	0·036
Steel axle, British specification .	0·320	0·756	0·186	0·038	0·035	0·051
Casting for hydraulic press . .	0·415	0·805	0·310	0·072	0·060	—
Casting for ship's stern frame .	0·393	0·730	0·164	0·055	0·048	traces
Gun steel, British	0·385	0·648	0·182	0·038	0·035	0·029
Forged shaft for ship's propeller .	0·345	0·555	0·096	0·040	0·042	0·055
Double shear steel	0·068	0·107	0·055	0·012	0·018	—
Spring steel, laminated, carriage .	0·645	0·732	0·044	0·036	0·032	0·045
Tool steel for heavy work . . .	0·750	0·468	0·238	0·021	0·018	0·022
Steel for swords, cutlasses, etc. .	0·980	0·255	0·124	0·017	0·020	—
Die steel for striking coins . .	1·085	0·264	0·133	0·011	0·009	traces
Tool steel for light work . . .	1·274	0·252	0·148	0·018	0·012	—
Cast steel for razors, surgical instruments, etc.	1·445	0·305	0·112	0·014	0·016	traces

	Carbon.	Manganese.	Silicon.	Phosphorus.	Sulphur.	Special Element.
Hadfield's manganese steel	0·875	13·330	0·068	0·030	0·047	—
Ordnance steel . . .	0·330	0·006	0·165	0·029	0·038	Ni, 3·94
Chrome projectile steel .	0·807	0·505	0·246	0·012	0·055	Cr, 5·74
Self-hardening tool steel .	0·650	0·100	0·608	traces	0·042	W, 9·87
American self-hardening tool steel	0·585	traces	0·034	0·009	0·014	Mo, 9·16
High speed steel . . .	0·612	0·268	0·214	0·012	0·019	W, 18·21 Cr, 3·85

558 *Recalescence of Steel.*—When ordinary steels, containing varying amounts of carbon, are allowed to cool from a temperature of about 1000°, it is found that at two or more temperatures

Manganese Silicate is often present in steels, sometimes visible to the naked eye, sometimes only under the microscope.

Ghosts are drawn out segregations of ferrite, high in sulphur, phosphorus, and sometimes carbon, which appear dark when etched.

COMPOUNDS OF IRON.

IRON AND OXYGEN.

560 Iron forms three oxides,

Iron monoxide, or ferrous oxide, FeO,
Magnetic oxide of iron, or ferroso-ferric oxide, Fe_3O_4,
Iron sesquioxide, or ferric oxide, Fe_2O_3.

The last two oxides occur in nature as minerals, and are used, not only as ores of iron, but also for medicinal purposes. Indeed, rust of iron (hydrated ferric oxide) is said to have been used as a medicine by Æsculapius, and Dioscorides also mentions *σκωρία σιδήρου* (probably iron-scales), as being a substance similar to rust, but possessing less active medicinal properties. Red hæmatite was termed blood-stone, and the same author states that this may be obtained artificially by igniting loadstone. Pliny terms iron rust or scale *squama ferri*, red iron ore *hæmatites*, and loadstone *magnes*, and describes the action of the latter upon iron. The reddish-yellow and red oxide of iron is called *crocus martis* by the Latin Geber. The later chemists describe various methods for its preparation, and in 1735 the artificially prepared black oxide was termed *ætheops martis.* For a long time these compounds were distinguished only by their different medicinal action. The supporters of the phlogistic theory considered them to be compounds of iron calx with various proportions of phlogiston. Thus, for instance, Scheele in 1777 states that the precipitate which an alkali produces in a solution of green vitriol when exposed to the air gives rise to crocus martis, and that fire-air or oxygen disappears. Hence he concludes that the precipitated calx gives up phlogiston in its conversion into crocus.

Lavoisier distinguished two oxides, æthiops and crocus. Other chemists, like Berthollet, believed that a large number of these oxides existed, and as late as 1811 the views of chemists on this subject were much divided. Gay-Lussac was the first to point out that in addition to the lower and higher oxides an intermediate compound exists; this was confirmed by Berzelius.[1]

Ferrous oxide acts as a basic oxide, yielding the readily oxidisable ferrous salts, FeR_2 (R = a univalent negative radicle), in which the metal is divalent. Ferric oxide acts as a basic oxide, yielding the ferric salts, FeR_3, in which the metal is trivalent; it has also a feeble acidic function, forming with many basic oxides a series of compounds known as the ferrites, $M^{II}O,Fe_2O_3$. The magnetic oxide does not correspond to any characteristic series of salts, but yields a mixture of ferrous and ferric salts when it is treated with acids. It may be regarded as a ferrous ferrite, FeO,Fe_2O_3. *Ferrates* are also known corresponding to the acidic oxide, FeO_3, which has not itself been prepared.

Iron Monoxide, or *Ferrous Oxide*, FeO, is obtained when hydrogen is passed over the sesquioxide heated to 300°, as a black powder which oxidises with incandescence on exposure, but loses this property after it has remained for twelve hours in an atmosphere of hydrogen (Siewert). The reduction of ferric oxide at a high temperature (700–1000°) by a mixture of hydrogen and steam yields a product which, although not pure, contains a high proportion of ferrous oxide.[2] This compound is formed also by the action of nitrous oxide on metallic iron at 200°.[3] When ferrous oxalate, FeC_2O_4, is heated at 150–160° in absence of air, a mixture of monoxide and metallic iron remains, as shown by Liebig's observation that the gas evolved consists of fifty-six parts of carbon monoxide and sixty-eight parts of carbon dioxide.[4] If ferrous oxalate is added to boiling caustic potash the monoxide is obtained as a black, velvety powder, which when washed with water in the air takes up oxygen (Böttger).

Ferrous Hydroxide, $Fe(OH)_2$, is formed when a pure ferrous salt is treated with caustic potash or soda freed from air. It is a white powder which, when washed with hot water and ether in absence of air, may be preserved in an atmosphere of hydrogen. As, however, it is difficult to obtain perfect absence of air, the ferrous hydroxide is usually obtained as a green, pulverulent mass.[1] It crystallises from solution in strong caustic soda in flat green prisms.[2]

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[1] See Wöhler and Balz, *Zeit. Elektrochem.*, 1921, **27**, 406.

[2] Hilpert and Beyer, *Ber.*, 1911, **44**, 1608; see also Sosman, *J. Washington Acad. Sci.*, 1917, **7**, 55.

[3] Sabatier and Senderens, *Compt. rend.*, 1892, **114**, 1429.

[4] See also Mixter, *Amer. J. Sci.*, 1913, [4], **36**, 556.

Ferrous hydroxide absorbs oxygen, assuming first a dirty-green colour which rapidly darkens and finally becomes brown owing to the formation of ferric hydroxide. On exposure of ferrous hydroxide to air, this process proceeds so rapidly that the mass sometimes becomes incandescent with formation of the sesquioxide. Owing to its affinity for oxygen ferrous hydroxide is a powerful reducing agent. It reduces nitrites and nitrates to ammonia, a reaction which may be used for the estimation of these substances.[3] It also absorbs carbon dioxide rapidly, and dissolves in acids with evolution of heat.

Ferrous hydroxide dissolves readily in acids to form the ferrous salts, which are produced also by the direct action of acids on metallic iron in the absence of oxidising agents, and by the reduction of the corresponding ferric salts. The anhydrous ferrous salts of colourless acids are usually colourless, but the corresponding hydrated salts possess a pale greenish-blue tint. The soluble salts possess a sweet, astringent, ink-like taste. Their neutral or acid solutions absorb oxygen slowly with formation of a ferric salt, part of which is precipitated in the form of basic salt when there is no excess of acid present. In presence of alkali, absorption of oxygen occurs rapidly, even at the ordinary temperature. Copper salts even in traces exert a marked catalytic effect in increasing the oxidation of ferrous salts.[4] In consequence of the ease with which they pass into a higher state of oxidation, the ferrous salts act as powerful reducing agents, and are largely employed for this purpose

Magnetic Oxide of Iron, Ferroso-ferric Oxide, or Triferric Tetroxide, Fe_3O_4, occurs in large masses as the mineral magnetite. It crystallises in octahedra, dodecahedra, and other combinations of the regular system. It has an iron-black colour, and a more or less strong metallic lustre. It frequently occurs in granular or amorphous masses, and is found also in marshes as an earthy mass known as ochreous iron ore (or in German *eisenmulm*). The pure crystallised mineral has a specific gravity of 5·18, whilst that of the granular and earthy material varies considerably, inasmuch as it contains magnesia, lime, and titanic oxide, and also often contains the iron in a more highly oxidised condition.

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[1] Schmidt, *Annalen*, 1840, **36**, 101.

[2] de Schulten, *Compt. rend.*, 1889, **109**, 266.

[3] Miyamoto, *Journ. Chem. Soc., Japan*, 1922, **43**, 397.

[4] Maquenne and Demoussy, *Compt. rend.*, 1920, **171**, 65.

The interesting observation that this ore has the power of attracting iron, and that by contact with it iron attains the same polar magnetic properties, was made at an early date. According to some, the name is derived from a certain Magnes, who was the first to observe this property, whilst according to others the name is derived from Magnesia, a town in Lydia also called Heraclea, where the mineral was first found. The latter explanation would seem to be the more probable, inasmuch as Plato and Theophrastus termed magnetite the Heraclean stone. Ferroso-ferric oxide does not always possess the magnetic properties exhibited by loadstone, although attracted by the magnet.

When iron is heated to redness in the air it becomes coated with an iron scale. This is a mixture or a compound of the monoxide and sesquioxide in varying proportions. The inner layer, which is blackish-grey, porous, brittle, and attracted by the magnet, has the composition $6FeO,Fe_2O_3$, and is not magnetic. The outer layer contains a large quantity of ferric oxide, is of a reddish colour, and is more strongly attracted by the magnet than the inner portion. When iron is quickly burnt in oxygen or in the oxy-hydrogen blowpipe, the oxide which is formed varies in composition according to the conditions of the experiment, although it approaches the composition of the magnetic oxide; the occurrence of this oxide has also been observed in smelting operations.

Magnetic oxide is obtained when excess of steam or carbon dioxide is passed over red-hot iron, but, on the other hand, when the oxides of iron are heated in a current of hydrogen or of carbon monoxide in excess, they are reduced to metal. Pure ferroso-ferric oxide may be prepared by reducing ferric oxide at 400° by a mixture of hydrogen and steam.[1] It is also obtained as black crystals by strongly heating ferric oxide with excess of sodium chloride[2] or by fusing iron with sodium sulphate. When the black oxide is dissolved in hydrochloric acid, or when a mixture of a ferrous and ferric salt is dissolved in the right proportions, and caustic alkali added to the solution, a black precipitate is obtained which dries to a brownish-black brittle mass giving a dark brown powder unalterable in the air. This hydroxide contains about 7 per cent. of water, and corresponds to the formula $Fe(OH)_2,Fe_2O_3$. It is attracted by the magnet, and may in this way be separated from any admixed sesquioxide.

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[1] Hilpert and Beyer, *Ber.*, 1911, **44**, 1608.

[2] Thompson, *Trans. Ceramic Soc.*, 1918, **17**, [2], 340.

Iron Sesquioxide, or *Ferric Oxide*, Fe_2O_3, is one of the most important ores of iron, occurring as red hæmatite, and as specular iron, crystallising in rhombohedra and scalenohedra, possessing a steel-grey colour. It also occurs under the name of micaceous iron in thin, red, translucent scales. This mineral is found in large quantity and in splendid crystals in the Island of Elba, of which Virgil[1] says: "Insula inexhaustis chalybdum generosa metallis." The crystals have a specific gravity of 5·19 to 5·25. The mineral martite is also a pure ferric oxide which crystallises in the same form as magnetic oxide, and is probably a pseudomorph of this mineral.

Ferric oxide can be prepared artificially in various ways. It is formed by igniting the hydroxide or any ferric salt containing a volatile acid, as a steel-grey, crystalline powder, which, like all other kinds of iron sesquioxide, gives a brownish-red powder when finely triturated, and has a specific gravity of 5·17. It may be obtained in small crystals by the action of the vapour of ferric chloride on heated lime (Daubrée), or by fusing ferric oxide and borax together and treating the cooled mass with hot dilute hydrochloric acid; also by passing a slow, steady stream of hydrogen chloride over the strongly ignited oxide (Deville). Artificial micaceous iron is prepared by heating a solution of ferrous sulphate and copper sulphate together for ten hours at a temperature of 210° (Wibel). Ferric oxide has also been observed in the crystalline state as a product in smelting operations, whilst crystals having the form of specular iron have been found in iron rust from a building some 700 to 800 years old. The ignited and natural ferric oxides dissolve only slowly in acids, the best solvent being a boiling mixture of eight parts of sulphuric acid and three parts of water. Ordinary ferric oxide is only very slightly paramagnetic and is not attracted by a small horse-shoe magnet. It has, however, been obtained in a more strongly magnetic form by the oxidation of ferrous hydroxide,[2] and Liversidge has described specimens of rust, which, although free from metallic iron and from ferrous oxide, are strongly magnetic. Heated in the electric furnace,[3] or in the oxy-hydrogen flame,[4] ferric oxide forms the magnetic oxide.

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[1] *Æn.* x. 17–34.

[2] Malaguti, *Compt. rend.*, 1862, 55, 350.

[3] Moissan, *ibid.*, 1892, 115, 1034.

[4] Read, *Journ. Chem. Soc.*, 1894, 65, 314.

The freezing point of ferric oxide, in an atmosphere of oxygen, is 1562–1565°.[1]

The colour of ferric oxide varies from bright yellow to black, depending upon the mode of preparation. The light-coloured varieties may be obtained by cautiously heating any of the sulphates of iron; other iron compounds yield darker products. All varieties become brown to dark violet on heating to 650° to 1000°, and above this temperature change to bluish-black or black.[2] A yellow form of anhydrous ferric oxide has also been made admixed with other substances such as aluminium oxide or calcium sulphate, which act as stabilising agents. Their removal results in agglomeration of the ferric oxide with consequent change of colour from yellow to red.[3] The yellow colour of bricks is due to this yellow modification of ferric oxide rendered stable by alumina.[4]

In addition to its use as an iron ore, ferric oxide is of service in a variety of other ways. Thus, the residue left in the process of distilling fuming sulphuric acid from green vitriol (Vol. I., p. 439), termed *colcothar* or *caput mortuum vitrioli*, is used largely as an oil-paint and also as a polishing powder; the least calcined portions, which are of a scarlet colour, are used as jewellers' rouge, whilst the more calcined portions, which have a bluish tint, are termed *crocus*, and are employed for polishing brass or steel. Noteworthy also is the employment of ferric oxide as catalyst in the contact process for the manufacture of sulphuric acid[5] (Vol. I., p. 437).

Hydrates of Ferric Oxide.—A very large number of different hydrates of ferric oxide have been prepared, or exist naturally as minerals, but the exact constitution of many of these is uncertain. Brown hæmatite or limonite has the composition $2Fe_2O_3,3H_2O$, göthite Fe_2O_3,H_2O, and hydrohæmatite, $2Fe_2O_3,H_2O$, all three being crystalline.

Muck[6] and Tommasi[7] obtained red hydrates by the precipitation of ferric salts with alkalis, and yellow hydrates by the oxidation of moist ferrous hydroxide or carbonate. By drying these at different temperatures Tommasi obtained various products which he regarded as definite hydrates, but van Bemmelen[1] has shown that all the "red" hydrates are in reality colloidal substances, the amount of water retained by them depending only on the pressure of the atmospheric aqueous vapour with which they are in equilibrium.[2]

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[1] Kohlmeyer, *Metallurgie*, 1909, **6**, 323.

[2] Hedvall, *Zeit. anorg. Chem.*, 1922, **121**, 217.

[3] Yoe, *J. Physical Chem.*, 1921, **25**, 196.

[4] Schoetz, *ibid.*, 1917, **21**, 570.

[5] Lunge and Pollitt, *Zeit. angew. Chem.*, 1902, **15**, 1105; Lunge and Reinhardt, *ibid.*, 1904, **17**, 1041; Keppeler and others, *ibid.*, 1908, **21**, 532, 577; *Zeit. physikal. Chem.*, 1908, **62**, 89.

[6] *Zeit. Chem.*, 1868, [2], **4**, 41.

[7] *Ber.*, 1879, **12**, 1929, 2334.

When freshly prepared red ferric hydroxide is heated with water under a pressure of about 5,000 atmospheres, it is converted into definite hydrates agreeing in composition with the naturally occurring minerals.[3] Between 30° and 42·5° limonite is formed, between 42·5° and 62·5 göthite, and above 62·5° hydrohæmatite.

Various pigments, notably red, yellow, and brown ochres, are made by heating the naturally occurring hydrates. The exact colour produced depends upon the degree of heating.[4]

Iron rust, when completely oxidised, is found to have a composition very close to that of limonite, viz. $2Fe_2O_3,3H_2O$; freshly formed rust, however, usually contains considerable quantities of ferrous hydroxide and carbonate.[5]

When ferric hydroxide is precipitated from solution, the quantities of salts and of water absorbed by it vary widely with the composition of the mother-liquor.[6] Arsenious acid forms an adsorption compound with freshly precipitated ferric hydroxide;[7] the latter substance, therefore, can be employed as an antidote in cases of arsenical poisoning.

Ferric hydroxide dissolves readily in acids to form the ferric salts, which may be obtained also by the action of oxidising agents on the corresponding ferrous salts. In the anhydrous state they are generally colourless; in the hydrated state they are yellow or brown. The soluble ferric salts possess a peculiar astringent taste, and they pass readily by reduction into the corresponding ferrous compounds.

Soluble Ferric Hydroxide.—When freshly precipitated ferric hydroxide is added to a solution of ferric chloride it dissolves, forming a dark red solution of basic ferric chloride, which may also be obtained by adding ammonium carbonate to a solution of ferric chloride until the precipitate first formed no longer redissolves. On dialysis of these solutions, hydrochloric acid and ferric chloride first pass through the membrane, and finally hydrochloric acid alone, leaving ferric hydroxide in solution in the dialyser (Graham). It is not possible, however, to remove all the chlorine in this manner; thus after 210 days the composition of the residual solution was found to correspond to the formula $82Fe(OH)_3,FeCl_3$.[1] According to Tribot and Chrétien,[2] the last portions of chlorine may be removed by subjecting the liquid to electrolysis, the colloidal solution being placed in a porous cell containing the cathode, the outer cell containing water, which is frequently renewed. Precipitated ferric hydroxide can be brought into colloidal solution by repeated washings in a centrifuge until free from the precipitating agent.[3] Colloidal ferric hydroxide can also be readily obtained by the action of potassium permanganate on a ferrous salt in absence of acid,[4] by boiling ferric nitrate with copper filings or fine dust,[5] or by dialysing a hot solution of ferric chloride.[6] The solution is used in medicine under the name of *Liquor Ferri Dialysati*.

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[1] *Rec. trav. chim.*, 1888, **7**, 37.

[2] See also Posnjak and Merwin, *Amer. J. Sci.*, 1919, [4], **47**, 311.

[3] Ruff, *Ber.*, 1901, **34**, 3417. Compare Fischer, *Zeit. anorg. Chem.*, 1910, **66**, 37.

[4] Bouchonnet, *Bull. Soc. chim.*, 1911, [4], **9**, 345; 1912, [4], **11**, 6.

[5] Moody, *Journ. Chem. Soc.*, 1906, **89**, 720.

[6] See Weiser, *J. Physical Chem.*, 1913, **17**, 536.

[7] Biltz, *Ber.*, 1904, **37**, 3138. See also Lockemann and Lucius, *Zeit. physikal. Chem.*, 1913, **83**, 735.

Colloidal ferric hydroxide solution is readily precipitated by electrolysis or by the addition of an electrolyte. As usually prepared, the colloid is positively charged, so that the efficiency of the precipitating electrolyte is dependent on the valency of its anion.[7] Negatively charged colloidal ferric hydroxide has also been made by adding the ordinary colloid or dilute ferric chloride solution to dilute sodium hydroxide solution with constant shaking.[8] The charge on a colloid is due to absorption of ions from solution and its sign will therefore depend on whether anions or cations are in excess in the layers of solution next to the particles. Non-electrolytes, as, for example, sugar and alcohol, do not bring about gelatinisation. The nature of the precipitated gel depends upon the conditions of precipitation.[9]

Ferric hydroxide forms a compound with sugar which is soluble in water. This fact is of great importance to the sugar refiners, as this compound destroys the crystallising power of sugar, and therefore increases the quantity of molasses formed. Hence raw sugar ought not to be brought into contact with iron, and the "char" employed for the decolorisation of the sugar should be as free as possible from the compounds of this metal.

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[1] Linder and Picton, *Journ. Chem. Soc.*, 1905, **87**, 1920.

[2] *Compt. rend.*, 1905, **140**, 144.

[3] Bradfield, *J. J., Amer. Chem. Soc.*, 1922, **44**, 965.

[4] Neidle and Crombie, *ibid.*, 1916, **38**, 2607.

[5] Cohen, *ibid.*, 1914, **36**, 19.

[6] Neidle and Barab, *ibid.*, 1917, **39**, 71.

[7] Freundlich, *Zeit. physikal. Chem.*, 1903, **44**, 131; Pappada, *Zeit. Chem. Ind. Kolloide*, 1911, **9**, 233.

[8] Powis, *Journ. Chem. Soc.*, 1915, **107**, 818.

[9] See Weiser, *J. Physical Chem.*, 1920, **24**, 277, 505.

561 Ferric hydroxide has feebly acidic properties, and combines with strong bases to form unstable salts, termed *ferrites.* The compound formed with the basic monoxides such as lime are analogous to ferrosoferric oxide, Fe_2O_3,FeO, which they resemble in being magnetic.

Alkali Ferrites.—Solutions of potassium and sodium ferrites are formed by boiling solutions of the corresponding ferrates, oxygen being evolved; the solution on standing deposits crystals of the ferrite, but these are very unstable and quickly decompose when removed from the alkaline liquid. A similar solution is obtained by boiling ferric hydroxide with concentrated caustic soda.[1] Sodium ferrite is also obtained by the electrolytic oxidation of iron in dilute caustic soda solution at low temperatures in complete absence of air, or by anodic oxidation of an alkaline solution of ferrous hydroxide or cathodic reduction of sodium ferrate solution, using platinum electrodes.[2] Sodium ferrite is produced also when ferric oxide is heated with sodium carbonate to bright redness, carbon dioxide being evolved. This reaction is made use of in the Löwig process for the manufacture of caustic soda from sodium carbonate.

Calcium Ferrite, Fe_2O_3,CaO.—This compound is obtained when an intimate mixture of 190 parts of ferric oxide and 66·5 parts of lime is heated to whiteness in a platinum vessel for several hours.[3] It forms a brittle mass of interlaced acicular crystals exceeding an inch in length, with a dark metallic lustre and magnetic properties. When ground it yields a brown powder, which is obtained also by precipitating a solution of ferric chloride, as nearly neutral as possible, with lime water or saccharate of lime, and igniting the precipitate. Other calcium ferrites, containing different proportions of the two oxides, have also been prepared,[4] but Sosman and Merwin[5] maintain that only two such compounds exist, namely, Fe_2O_3,CaO and $Fe_2O_3,2CaO$, the former giving deep red crystals and the latter black.

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[1] Haber and Pick, *Zeit. Elektrochem.*, 1901, **7**, 215, 724.

[2] Grube and Gmelin, *ibid.*, 1920, **26**, 459.

[3] Percy, *Phil. Mag.*, 1873, [4], **45**, 455.

[4] Hilpert and Kohlmeyer, *Ber.*, 1909, **42**, 4581.

[5] *J. Washington Acad. Sci.*, 1916, **6**, 532. See also Campbell, *J. Ind. Eng. Chem.*, 1919, **11**, 116.

Magnesium Ferrite, Fe_2O_3,MgO, occurs in nature crystallising in black octahedra as magnoferrite, and is obtained artificially by the ignition of a mixture of the two oxides in a current of hydrogen chloride, or by the precipitation of a mixture of ferric chloride and magnesium chloride with a quantity of caustic soda insufficient to throw down the whole. Many analogous compounds can be prepared in a similar way.[1]

Zinc Ferrite, Fe_2O_3,ZnO, was obtained by Ebelmen in black octahedra by strongly igniting both oxides together with boron trioxide. The mineral franklinite has a similar composition.

562 *Ferric Acid*, H_2FeO_4.—This compound, like manganic acid, is not known in the free state. In the year 1702 Stahl noticed that when iron is fused with saltpetre and the solid mass lixiviated, or when a solution of iron in nitric acid is added to concentrated potash-ley, an amethyst or purple-red coloured solution is formed. Exactly a century afterwards Eckeberg published his memoir on "Yttria," in which he states that when gadolinite is fused with potash and the fused mass extracted with water, the solution possesses a dark purple-red colour, due to iron and not to manganese. The potassium ferrate formed in these circumstances was more carefully examined by Fremy.[2] It is prepared by igniting iron filings or iron oxide with saltpetre or caustic potash, or a mixture of both. The formation of the compound may be readily shown by heating a mixture of one part of powdered iron with two parts of saltpetre in a small glass bulb, over a Bunsen burner. After a few minutes the mass becomes red hot, and when cold the residue is dissolved in water.[3] The purple solution is obtained also by passing chlorine through a strong solution of caustic potash in which ferric hydroxide is suspended (Fremy).

Ferrates are readily produced also by the electrolytic oxidation of iron in caustic potash or soda solution. When iron is used as anode in concentrated caustic potash or soda solution and a low current density employed, all varieties of iron yield ferrate, but the yield is greatest with cast iron, smallest with wrought iron, and increases with the temperature. A good yield is obtained by immersing two large iron plates in concentrated alkali at 70° and making these alternately cathode and anode, the reversal taking place four times per minute. The iron plates become passive during the process.[1] A better yield is obtained by imposing an alternating current on the direct current and working at a temperature not exceeding 50°, above which there is appreciable decomposition of the ferrate with evolution of oxygen and precipitation of the hydroxide.[2]

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[1] List, *Ber.*, 1878, **11**, 1512.

[2] *J. Pharm.*, 1841, **27**, 97.

[3] Hofmann, *Ber.*, 1869, **2**, 239.

The concentrated potassium ferrate solution is almost black, and on addition of more potash deposits a reddish-brown precipitate, which is very unstable, but may be preserved by drying on a porous plate and sealing in a glass tube. As already mentioned, the solution decomposes on boiling, with evolution of oxygen and formation of a yellow solution of potassium ferrite, from which ferric hydroxide readily separates. Nitric acid and sulphuric acid yield a ferric salt with evolution of oxygen, whilst with hydrochloric acid chlorine is evolved.

Barium Ferrate, $BaFeO_4,H_2O$, is the most stable of the salts, and is obtained in the form of a dark red powder by precipitating a solution of the potassium or sodium salt with barium chloride. It is fairly stable, and yields a red solution with acetic acid. It is not decomposed by dilute sulphuric acid in the cold, but at once yields ferric and barium salts with hydrochloric and nitric acids, with evolution of chlorine and oxygen respectively.[3]

IRON AND HYDROGEN.

563 The absorption of hydrogen by iron and its diffusion through the metal have already been discussed.

By the action of zinc ethyl, $Zn(C_2H_5)_2$, on anhydrous ferrous iodide in presence of ether, Wanklyn and Carius found that a mixture of ethylene, ethane, butane, and hydrogen is evolved, and that the residue on washing with ether yields a metallic powder resembling iron, which evolves hydrogen on heating and is decomposed by water with evolution of hydrogen, leaving a residue of metallic iron and ferrous oxide.[4] It is possible that this product contains a compound of hydrogen and iron, but further investigation is needed.

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[1] Haber and Pick, *Zeit. Elektrochem.*, 1901, **7**, 215, 712, 724.

[2] Grube and Gmelin, *ibid.*, 1920, **26**, 153.

[3] Baschieri, *Gazz.*, 1906, **36**, ii, 282.

[4] *Annalen*, 1861, **120**, 74.

IRON AND THE HALOGENS.

564 *Ferrous Fluoride*, FeF_2, is obtained in colourless or greenish prisms, $FeF_2,8H_2O$, by dissolving iron in hydrofluoric acid and evaporating; these crystals decompose when gently heated, leaving the anhydrous salt; this is formed also when iron or ferric chloride is heated in dry hydrogen fluoride, and crystallises in colourless rhombic prisms.

A number of double fluorides with ammonium and alkali fluorides have been prepared.

Ferric Fluoride, FeF_3, is obtained by dissolving the hydroxide in hydrofluoric acid, colourless crystals of $2FeF_3,9H_2O$ separating out from the colourless solution on evaporation. On heating this at 100° the hexa-hydrate, $2FeF_3,6H_2O$, is obtained. The formula $FeF_4(OH)_2(HF)_2,4H_2O$ has been proposed for this compound in order the more easily to account for the following reactions[1]: (1) Only one-third of the fluorine enters into double decomposition with barium chloride in aqueous solution. (2) When the solid is boiled with alcohol one-third of the fluorine is rapidly eliminated as hydrogen fluoride, but the remainder is lost very slowly. (3) At 95°, the salt loses water rapidly and proportionally to the loss of fluorine until one-third has been eliminated, when no more water is lost. (4) Prolonged heating at 95° yields an oxyfluoride in accordance with the equation

$$FeF_4(OH)_2(HF)_2 = FeOF_4 + H_2O + 2HF.$$

The anhydrous salt is obtained by heating the hexahydrate in a stream of hydrogen fluoride or by strongly heating iron, ferric oxide, or chloride in a stream of the gas. It does not fuse even at 1000°, and forms ferric oxide when heated in the air.[2]

Several double salts with the alkali fluorides are known.

Ferroso-ferric Fluoride, $Fe_3F_8,10H_2O$, has been described.[3]

Ferrous Chloride, $FeCl_2$, is obtained by passing chlorine over iron filings (Thénard), but as a small quantity of ferric chloride is generally formed, even when an excess of iron is present, it is preferable to pass hydrogen chloride over iron filings or iron wire heated to redness (Wöhler and Liebig), or to reduce ferric chloride by heating it in a stream of pure hydrogen. Ferrous chloride is deposited in colourless, shining scales, which, according to Sénarmont, are six-sided. It has a specific gravity of

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[1] Recoura, *Compt. rend.*, 1912, **155**, 655. [2] Poulenc, *ibid.*, 1892, **114**, 941.
[3] Deussen, *Monatsh.*, 1907, **28**, 163.

2·528 (Filhol), and is very deliquescent, dissolving readily in water and alcohol. It fuses at a red heat, and volatilises at a yellow heat, when its vapour has a density of 6·38–6·67,[1] whilst at 1300–1500° it acquires the normal value of 4·3.[2]

When heated in the air it oxidises to ferric chloride, which volatilises, ferric oxide remaining behind:

$$12FeCl_2 + 3O_2 = 8FeCl_3 + 2Fe_2O_3.$$

When heated in a current of steam, magnetic oxide is formed:

$$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2.$$

When iron is dissolved in hydrochloric acid, and the solution concentrated in absence of air, bluish, transparent, monoclinic crystals of $FeCl_2,4H_2O$ are obtained; these have a specific gravity of 1·93, and deliquesce and become greenish coloured on exposure to the air, but effloresce at ordinary temperatures when kept over oil of vitriol. If a solution of this salt is evaporated with sal-ammoniac in absence of air, and the solid mass is heated in a flask until the whole of the sal-ammoniac is volatilised, the residue is anhydrous ferrous chloride. Hydrates with 1, 2, and 6 H_2O have also been obtained. Like other soluble ferrous salts, the solution of ferrous chloride absorbs nitric oxide, forming a dark, greenish-brown solution, possibly containing the unstable compound $FeCl_2,NO$ (p. 1293). The anhydrous chloride readily absorbs ammonia with evolution of heat and formation of a white powder (Faraday), which has the composition $FeCl_2,6NH_3$, gives off ammonia at 100°, and at higher temperatures yields ammonium chloride, iron nitride, and nitrogen.[3] Two other ammoniates exist, namely $FeCl_2,2NH_3$, and $FeCl_2,NH_3$,[4] the former being produced by heating the hexammoniate in hydrogen at 100°.

A number of double chlorides have been prepared.

Ferroso-ferric Chloride, $Fe_3Cl_8,18H_2O$.—Magnetic oxide of iron dissolves in concentrated hydrochloric acid, forming a yellow liquid, which on concentration over sulphuric acid deposits the above salt in opaque yellow deliquescent crystalline crusts.

Ferric Chloride, $FeCl_3$.—The aqueous solution of this salt was known to Glauber under the name of *oleum martis.* He obtained it in the dry state by dissolving iron in hydrochloric acid and evaporating the solution in a flask: "*In fundo* there remains a blood-red *massa*, which is as hot to the tongue as fire. It must be well-kept from the air, otherwise it liquefies to a yellow *oleum.*"

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[1] Meyer, *Ber.*, 1884, **17**, 1335.

[2] Nilson and Pettersson, *Journ. Chem. Soc.*, 1888, **53**, 827.

[3] Fowler, *ibid.*, 1901, **79**, 288. Compare Girardet, *Bull. Soc. chim.*, 1910, **7**, 1028.

[4] See Biltz and Hüttig, *Zeit. anorg. Chem.*, 1919, **109**, 89.

Anhydrous ferric chloride is obtained by heating iron wire in a current of dry chlorine gas at a moderate red heat, when rapid combination with ignition takes place, ferric chloride being deposited. It is produced also when hydrogen chloride is passed over heated amorphous ferric oxide, and is not infrequently found in the craters of volcanoes.

Ferric chloride forms iron-black iridescent plates, or sometimes large hexagonal tablets, which exhibit a red colour by transmitted light, and a green, metallic lustre by reflected light. It is very deliquescent, and easily soluble in water, alcohol, or ether. It volatilises at about 28°, but under pressure melts at 301°. Between 321° and 442° its vapour density is practically constant and agrees with the double formula Fe_2Cl_6. At higher temperatures it is dissociated into ferrous chloride and chlorine, $Fe_2Cl_6 \rightleftharpoons Fe_2Cl_4 + Cl_2$, and on raising the temperature to about 1050° the double ferrous chloride molecules are dissociated into single.[1] When dissolved in boiling alcohol or ether it appears to have a molecular weight corresponding to the formula $FeCl_3$.[2]

Ferric chloride forms with ammonia at the ordinary temperature the compound $FeCl_3,6NH_3$, which loses NH_3 on exposure to air, yielding the pentammoniate, $2NH_3$, when heated at 100°, leaving the tetrammoniate; at higher temperatures, it gives ammonium chloride.[3] It also absorbs nitrosyl chloride, yielding a dark-coloured, deliquescent compound, $FeCl_3,NOCl$, and unites with nitric oxide at the ordinary temperature to form several unstable compounds, whilst at higher temperatures it is reduced by the gas to ferrous chloride.[4] It is also reduced to ferrous chloride by heating in a stream of hydrogen. When heated in a current of steam it is decomposed into ferric oxide and hydrogen chloride, and when heated in oxygen, chlorine is evolved, ferric oxide remaining. Anhydrous ferric chloride, intimately mixed with calcium and heated to dull redness, yields metallic iron.[1]

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[1] Friedel and Crafts, *Compt. rend.*, 1888, **107**, 301. See also Grüneweld and Meyer, *Ber.*, 1888, **21**, 687.

[2] Muller, *Compt. rend.*, 1894, **118**, 644.

[3] Miller, *Amer. Chem. J.*, 1895, **17**, 570.

[4] Besson, *Compt. rend.*, 1889, **108**, 1012; Thomas, *ibid.*, 1895, **120**, 447; **121**, 128.

Ferric chloride forms compounds with a large number of organic compounds.[2] The compound with ether is a dark red, very deliquescent solid which is decomposed quantitatively on heating at 100°, yielding pure ethyl chloride and the oxychloride, FeOCl.[3]

$$FeCl_3,(C_2H_5)_2O = 2C_2H_5Cl + FeOCl.$$

For the purpose of obtaining a solution of ferric chloride, the hydroxide may be dissolved in hydrochloric acid and the liquid evaporated in order to drive off excess of acid, or a solution of ferrous chloride may be heated with the requisite quantity of hydrochloric acid and the heated solution oxidised by addition of nitric acid. A solution of ferric chloride is, however, best prepared by dissolving iron wire in hydrochloric acid, as described under the preparation of ferrous chloride, and then passing chlorine into this solution until, after standing for some time, it smells strongly of the gas. The excess of chlorine is then displaced by passing a current of carbon dioxide through the warm liquid. A concentrated solution of ferric chloride has a dark brown colour and an oily consistency. On dilution it becomes limpid, and has a slightly yellow colour. It is readily hydrolysed in solution to the hydroxide and hydrochloric acid,

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

[illegible] to the formation of free acid, the electrical conductivity of the solution increases and measurement of the rate shows that it is gradual. This has been explained by assuming that the hydrolysis takes place in stages, each chlorine atom being hydrolysed in turn. It is, however, more probable that the hydrolysis occurs immediately on dilution and that the free acid produced is completely adsorbed by the colloidal particles of the hydroxide. These particles are at first very small, but they gradually increase in size so that their total surface becomes less and less and the adsorbed acid is thus gradually liberated.[4] Very dilute solutions of ferric chloride are practically colourless when freshly prepared, but they gradually darken in colour, finally becoming a dark brown owing to the separation of the hydroxide. In extremely dilute solution the hydrolysis is so complete that owing to the absence of ferric ions no coloration is produced with potassium ferrocyanide.

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[1] Hackspill, *Bull. Soc. chim.*, 1907, 1, 895.

[2] See Gangloff and Henderson, *J. Amer. Chem. Soc.*, 1917, **39**, 1420.

[3] Forster, Cooper, and Yarrow, *Journ. Chem. Soc.*, 1917, **111**, 809.

[4] Wagner, *Monatsh.*, 1913, **34**, 95, 931. See also Quartaroli, *Gazz.*, 1915, **45**, i, 139.

Four different hydrates of ferric chloride have been described by Roozeboom :[1] $FeCl_3,6H_2O$, melting at 37° ; $2FeCl_3,7H_2O$, melting at 32·5° ; $2FeCl_3,5H_2O$, melting at 56° ; and $FeCl_3,2H_2O$, melting at 73·5°. Solutions which contain more iron than corresponds to the formula $FeCl_3,2H_2O$ deposit the anhydrous salt when evaporated above the temperature of 66°. A deliquescent compound, $FeCl_3,HCl,2H_2O$, is formed by the action of hydrochloric acid on the pentahydrate, whilst similar compounds with $4H_2O$ and $6H_2O$ are also known.[2] The aqueous solution of the normal chloride is decomposed on heating, the more easily the more dilute the solution is, an insoluble oxychloride or soluble ferric hydroxide being produced according to the concentration of the liquid.[3]

The solutions of ferrous and ferric chlorides have long been used in medicine. An alcoholic solution of ferric chloride was formerly employed as a quack medicine of repute, known by the name of Lamotte's golden drops. This solution loses its colour when exposed to light,[4] ferrous chloride being formed, the latter compound separating, when the solution is not too dilute, in fine green crystals, $FeCl_2,2H_2O$. Dilute solutions of ferric chloride in ether are reduced to ferrous chloride almost immediately on exposure to sunlight, the chlorine attacking the ether. Concentrated solutions are reduced more slowly, and a black organic compound containing iron is also formed.[5]

Ferric chloride forms garnet-red, crystalline double salts with the chlorides of the metals of the magnesium and alkali groups, such as $FeCl_3,MgCl_2,H_2O$; $FeCl_3,2KCl,H_2O$; and $FeCl_3,2NH_4Cl,H_2O$. These are decomposed by water, and a mixture of the last salt with an excess of sal-ammoniac is termed iron sal-ammoniac; it was formerly obtained by sublimation of a mixture of iron oxide and ammonium chloride, and is mentioned by "Basil Valentine." Iron sal-ammoniac crystallises in yellow or bright red, transparent, regular crystals from a dilute solution of ferric chloride; these contain a varying amount of iron, and are very hygroscopic.

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[1] *Zeit. physikal. Chem.*, 1892, **10**, 477.

[2] Sabatier, *Bull. Soc. chim.*, 1881, [2], **36**, 197; Roozeboom and Schreinemakers, *Zeit. physikal. Chem.*, 1894, **15**, 588.

[3] Compare Malfitano and Michel, *Compt. rend.*, 1907, **145**, 187, 1275; 1908, **146**, 338; 1908, **147**, 803; Michel, *ibid.*, 1908, **147**, 1062, 1288; Cameron and Robinson, *J. Physical Chem.*, 1907, **11**, 690.

[4] See Benrath, *J. pr. Chem.*, 1905, **72**, 220; 1909, **80**, 283.

[5] Puxeddu, *Gazz.*, 1920, **50**, i, 154.

Iron Oxychlorides.—These compounds are formed in various ways. Some are soluble whilst others are insoluble in water. When freshly precipitated ferric hydroxide is added to a solution of ferric chloride, it dissolves in considerable quantity, and a dark red liquid is obtained, which, to one molecule of chloride, may contain twenty or more molecules of oxide, and this on dialysis furnishes Graham's soluble oxide. These solutions may be diluted or warmed without any precipitation of ferric oxide. Many acids and salts, however, precipitate either ferric hydroxide or a basic chloride from these solutions, which latter is again soluble in water. If ferric chloride be incompletely precipitated with alkalis, a precipitate is obtained which is soluble in water when it does not contain more oxide than is indicated by the formula $FeCl_3,5Fe(OH)_3$.

Insoluble basic ferric chlorides are formed, in the first place, by the oxidation of ferrous chloride in the air; secondly, by roasting iron in the presence of hydrochloric acid or a chloride; and, thirdly, by boiling a solution of ferric chloride for some time. The composition and colour of these salts vary according to the mode of preparation. They are generally sparingly soluble in hydrochloric acid.

Ferrous Bromide, $FeBr_2$.—When bromine vapour is passed over iron heated to dull redness, heat is evolved, and a yellowish, crystalline deposit of ferrous bromide is formed (Liebig). It readily absorbs ammonia, yielding a hexammoniate, $FeBr_2,6NH_3$, which, on warming, dissociates, yielding a di- and then a mon-ammoniate.[1] An aqueous solution of ferrous bromide can easily be obtained by dissolving iron in hydrobromic acid; on crystallising, bluish-green, rhombic tablets are deposited, having the composition $FeBr_2,6H_2O$ (Löwig).

Ferric Bromide, $FeBr_3$.—This is obtained in the form of dark red crystals by heating iron in an excess of bromine vapour. When heated in absence of air it fuses, and a part may be sublimed without decomposition, another portion, however, being decomposed into ferrous bromide and free bromine. The bromide deliquesces on exposure to air, and the solution, which may be simply obtained by dissolving the hydroxide in hydrobromic acid, decomposes on evaporation, with formation of insoluble basic bromides. By concentrating the solution over sulphuric acid, however, dark green needles of the hexahydrate, $FeBr_3,6H_2O$, are obtained. Like the chloride, the solution of the bromide dissolves ferric hydroxide readily with formation of soluble oxybromides. It forms double salts with certain of the alkali bromides.

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[1] Ephraim, *Ber.*, 1912, **45**, 1322.

An unstable ferric chlorobromide, $FeCl_2Br$, is formed by the direct union of ferrous chloride and bromine.[1]

Ferrous Iodide, FeI_2, is obtained by triturating iodine with a slight excess of iron filings, or by heating the latter in a covered porcelain crucible to redness, small quantities of iodine being gradually added; as soon as the whole mass becomes red-hot, a large quantity of iodine is thrown in, and the crucible is heated until iodine vapour ceases to be given off. On allowing the crucible to cool it is found that a further evolution of iodine vapour takes place, probably owing to the fact that the fused mass contains an unstable ferric iodide, which decomposes on cooling. The solid residue is a grey lamino-crystalline mass, which melts at 177°.[2] If a mixture of iodine and iron filings be warmed with water, these elements combine with evolution of heat, and a colourless aqueous solution of ferrous iodide is obtained, which on exposure to the air oxidises readily with separation of iodine. This decomposition is prevented by the addition of sugar. Ferrous iodide crystallises with $5H_2O$. The anhydrous salt absorbs ammonia, giving a hexammoniate, $FeI_2,6NH_3$, which dissociates, yielding the diammoniate on heating.[3]

Ferrous Perchlorate, $Fe(ClO_4)_2,6H_2O$, is the only iron salt of the oxy-acids of chlorine which is stable in the solid state. It is obtained by the double decomposition of ferrous sulphate and barium perchlorate (Serullas), or by dissolving iron in dilute perchloric acid (Roscoe). It forms pale green deliquescent crystals, which give off water at 100°, and decompose at a higher temperature.

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[1] Lenormand, *Compt. rend.*, 1893, **116**, 820.

[2] Wanklyn and Carius, *Annalen*, 1861, **120**, 69.

[3] Biltz and Hüttig, *Zeit. anorg. Chem.*, 1919, **109**, 89.

IRON AND SULPHUR.

565 *Iron Subsulphide*, Fe_4S_3, is formed when iron is heated in the vapour of carbon disulphide, as a crystalline mass of specific gravity 6·957. It dissolves in dilute acids with evolution of hydrogen and sulphuretted hydrogen.[1]

Iron Monosulphide, or *Ferrous Sulphide*, FeS, occurs as troilite in small quantities in many meteorites, and is formed readily by the direct union of the elements. Iron wire burns in sulphur vapour with a bright light, and a roll of sulphur penetrates red-hot wrought iron and steel, but not cast iron, with formation of the molten sulphide.[2] In order to prepare this substance a mixture of three parts of iron filings and two parts of sulphur is thrown gradually into a red-hot crucible. The porous black mass obtained melts at a higher temperature, with separation of sulphur, if any higher sulphides have been formed, but as a rule the artificial sulphide contains an excess of iron, and this is removed by heating with excess of sulphur. For the preparation of the monosulphide, Berzelius recommends Gahn's process, namely, stirring a white-hot rod of iron in molten sulphur. The sulphide which is formed fuses and falls to the bottom of the crucible. The operation is continued as long as any free sulphur remains.

Pure monosulphide of iron is a yellowish, crystalline mass having a metallic lustre, and melting at 1300°.[3] It has a specific gravity of 4·69, is not magnetic, and does not lose sulphur when ignited in an atmosphere of hydrogen, or when raised to a white heat in the absence of air. It is readily decomposed by hydrochloric and dilute sulphuric acids, forming sulphuretted hydrogen, and is used as a source of this gas in the laboratory. As the sulphide usually contains free iron, the gas thus produced is always contaminated with hydrogen. When heated in the air it oxidises, being converted partly into ferrous sulphate, whilst at a high temperature sulphur dioxide and ferric oxide are formed. It is also oxidised when heated in steam, magnetic oxide being produced and hydrogen and hydrogen sulphide liberated:

$$3FeS + 4H_2O = Fe_3O_4 + 3H_2S + H_2.$$

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[1] Gautier and Hallopeau, *Compt. rend.*, 1889, **108**, 806.

[2] Evain, *Ann. Chim. Phys.*, 1824, [2], **25**, 106.

[3] Treitschke and Tammann, *Zeit. anorg. chem.*, 1906, **49**, 320. Compare Allen, Crenshaw, Johnston, and Larsen, *Amer. J. Sci.*, 1912, **33**, 169.

Ammonium sulphide precipitates ferrous sulphide from solutions of ferrous salts as a black, amorphous, hydrated mass. It is not precipitated from a neutral solution of a ferrous salt owing to the formation of acid, in which it is soluble,

$$FeSO_4 + H_2S \rightleftharpoons FeS + H_2SO_4.$$

So sensitive is the equilibrium that ferrous sulphide has been suggested as an indicator in acidimetry. A small crystal of ferrous ammonium sulphate is added to the liquid to be titrated and hydrogen sulphide is bubbled through it. If the solution is alkaline, it becomes black owing to the formation of ferrous sulphide. On the addition of acid, the black colour disappears immediately the alkali is neutralised. It is as sensitive as phenolphthalein or methyl-orange, and is particularly useful when dealing with coloured liquids or working in a bad light.[1] By the addition of a salt of a weak acid, for example, sodium acetate, to a solution of a ferrous salt, the ionisation of the strong acid may be so depressed that ferrous sulphide is precipitated on passing hydrogen sulphide.

Ferrous sulphide forms double sulphides.[2] Some of these occur in nature, for example, magnetic pyrites, $5FeS,Fe_2S_3$; pentlandite, $2FeS,NiS$, and marmatite, $FeS,4ZnS$.

If seven parts of iron filings and four parts of sulphur are rubbed up to a paste with water, a black sulphide is produced with evolution of heat. In this form it oxidises very quickly in the air with rise of temperature which, when the mixture is in large quantity, may lead to incandescence. Hence, according to Lemery, artificial volcanoes may be formed if several pounds of the above mixture be buried in the earth. The black, amorphous sulphide is formed also by the reduction of ferric oxide or its salts in presence of sulphates and decomposing organic matter. This is the cause of the black deposit found in drains, as well as in the excrement, when iron is used as a medicine.

Iron Sesquisulphide, or *Ferric Sulphide*, Fe_2S_3, does not occur pure in the mineral kingdom, but probably forms a constituent of magnetic pyrites and copper pyrites. It is obtained by the action of ammonium sulphide solution on a solution of a ferric salt, so long as alkali is in excess,[3] but if the ferric salt be in excess a mixture of ferrous sulphide and sulphur is formed. It is produced also by the action of sulphuretted hydrogen on moist ferric hydroxide or ferric hydroxide suspended in water. The product is a black mass which, when moist in absence of air, is transformed into a mixture of the disulphide and ferrous sulphide,

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[1] Houben, *Ber.*, 1919, **52**, [*B*], 1613.

[2] See Houdard, *Compt. rend.*, 1907, **144**, 801; Bornemann and Schreyer, *Metallurgie*, 1909, **6**, 619; Röhl, *Iron Steel Inst. Carnegie Mem.*, 1912, **4**, 28; Horsch, *Bull Soc. chim.*, 1920, [4], **27**, 777.

[3] See Stokes, *J. Amer. Chem. Soc.*, 1907, **29**, 304; Malfatti, *Zeit. anal. Chem.*, 1908, **49**, 133.

$$Fe_2S_3 = FeS + FeS_2.$$

This reaction occurs in the presence of excess of hydrogen sulphide and takes about a week at ordinary temperatures, but only a few hours at 60°. It is prevented by the presence of a small quantity of alkali in the absence of air. Exposed to air in the presence of alkali, the mass becomes light yellow in colour, sulphur being deposited.[1] Since coal-gas always contains small quantities of ammonia, ferric sulphide is the chief product formed in its purification from sulphuretted hydrogen[2] (Vol. I, p. 882). In the dry way, it is formed by gently heating sulphur and iron together, as well as by the action of sulphuretted hydrogen on ferric oxide at a temperature not above 100°. The sulphide obtained at a red heat forms a yellow, non-magnetic mass which has a specific gravity of 4·4, and is decomposed by dilute hydrochloric acid into sulphuretted hydrogen, ferrous sulphate, and iron disulphide. Iron sesquisulphide forms compounds with the other sulphides.[3]

Potassium Ferric Sulphide, $K_2Fe_2S_4$, is obtained when iron filings, sulphur, and potassium carbonate are heated together, and the residue is extracted with water. The purple-coloured, glistening, needle-shaped crystals thus obtained have a specific gravity of 2·863, and burn when heated in the air, but when ignited in a current of hydrogen are converted without change of form into the black compound, $K_2Fe_2S_3$.

Sodium Ferric Sulphide, $Na_2Fe_2S_4,4H_2O$, is obtained in a similar way and forms brown, microscopic needles. It is also formed by the addition of a ferric salt to sodium sulphide solution or by the action of the excess of sodium polysulphide on a ferrous salt in solution.[4] It is found in the "black ash" liquors obtained in the manufacture of soda by the Leblanc process.

Silver Ferric Sulphide, $Ag_2Fe_2S_4$, is a dark brownish-black, crystalline powder obtained by the action of silver nitrate solution on the potassium compound.

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[1] Rodt, *Zeit. angew. Chem.*, 1916, 29, i, 422; Mecklenburg and Rodt, *Zeit. anorg. Chem.*, 1918, 102, 130.

[2] Gedel, *J. für Gasbeleuchtung*, 1905, 48, 400; Stokes, *loc. cit.*

[3] Schneider, *Pogg. Ann.*, 1869, 136, 460; Preis, *J. pr. Chem.*, 1869, 107, 10; Malfatti, *Zeit. anal. chem.*, 1909, 48, 352.

[4] Mecklenburg and Rodt, *loc. cit.*

Cuprous Ferric Sulphide, Cu_2S,Fe_2S_3, occurs as the mineral copper pyrites. It may be made by shaking an ammoniacal solution of cuprous chloride with potassium ferric sulphide until all the copper has been precipitated.

Magnetic pyrites or *pyrrhotite* may be regarded as a compound of the mono- and sesqui-sulphides, but is probably not a definite compound but a solid solution of sulphur in ferrous sulphide.[1] Its composition varies between $5FeS,Fe_2S_3$ and $6FeS,Fe_2S_3$. It crystallises in hexagonal plates, usually, however, occurring in the massive state, having a brownish-yellow or brassy colour; it is attracted by the magnet, sometimes being itself magnetic. Its specific gravity varies from 4·4 to 4·7, and it frequently contains as much as 5·5 per cent. of nickel, the latter metal being obtained in Canada from this source in considerable quantities.

Iron Disulphide, FeS_2, occurs very widely distributed as iron pyrites. This mineral was known in early times, but was not distinguished from copper pyrites, both being known under the name of πυρίτης. Agricola considered these as two varieties of the same mineral.

Iron pyrites is found in all geological formations; it crystallises usually in cubes or pentagonal dodecahedra,[2] but occurs also in many other forms and combinations of the regular system, no fewer than sixty-nine different forms having been described. It is frequently found in spherical, botryoidal, or stalactitic masses, being formed by the action of organic matter on water which contains iron sulphate in solution. Hence it is frequently found in peat and coal in crystalline masses often possessing the form of the original organic matter, such as wood, roots, etc. It is likewise found in chalk cliffs, in similar concretionary forms. In the pure state, iron pyrites has a brass-yellow colour, and a specific gravity of 5·185. It is very hard, giving sparks when struck with steel, for which purpose it was formerly employed.

Iron disulphide occurs also as marcasite forming bright brass-coloured, rhombic crystals with a specific gravity of 4·68 to 4·85. This is also widely diffused, and occurs in various forms, especially in lignite beds. When broken, it exposes an almost white surface and is therefore also known as white iron pyrites. The fracture exhibits a fibrous structure radiating from a point, hence the name radiated pyrites, which is also applied to the mineral. Whereas iron pyrites is quite permanent in the air, marcasite is oxidised to ferrous sulphate and becomes disintegrated. When heated to between 400° and 500°, marcasite is slowly transformed into pyrites and the change is not reversible. In order to account for the differences in properties between pyrites and marcasite, the following constitutions have been suggested for them :[1]

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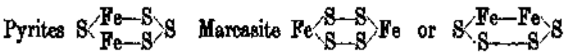
[1] Allen, Crenshaw, Johnston, and Larsen, *Amer. J. Sci.*, 1912, [4], 33, 169.

[2] See Pöschl, *Zeit. Kryst. Min.*, 1911, 48, 572.



$$\text{Pyrites } S\langle{}^{Fe-S}_{Fe-S}\rangle S \quad \text{Marcasite } Fe\langle{}^{S-S}_{S-S}\rangle Fe \quad \text{or} \quad S\langle{}^{Fe-Fe}_{S-\!-\!-S}\rangle S$$

Iron disulphide may be obtained artificially by gently heating the monosulphide with sulphur, or by passing sulphuretted hydrogen over the oxides or chlorides of iron heated to redness. It is also produced by boiling precipitated ferrous sulphide with flowers of sulphur or by adding sodium trisulphide slowly to a boiling solution of ferrous sulphate when sulphur is also liberated.[2] When an intimate mixture of ferric oxide, sulphur, and sal-ammoniac is heated slowly above the temperature at which the latter compound volatilises, the disulphide is obtained in small, brass-yellow octahedra and cubes (Wöhler). Crystalline pyrites is formed also when carbon disulphide vapour acts upon ferric oxide (Schlagdenhauffen), and when ferric chloride is heated with phosphorus pentasulphide.[3] Iron pyrites and marcasite may be produced artificially also by the action of hydrogen sulphide on ferric sulphate solution.[4] Iron disulphide is not magnetic, and is not attacked by dilute acids or sulphuric acid, but readily dissolves in nitric acid with separation of sulphur. There is some evidence showing that the iron in iron pyrites is in the ferrous condition.[5]

Ferrous Sulphite, $FeSO_3$.—When iron is dissolved in aqueous sulphurous acid in absence of air, no gas is evolved, and the solution contains ferrous sulphite and ferrous thiosulphate :

$$2Fe + 3H_2SO_3 = FeSO_3 + FeS_2O_3 + 3H_2O.$$

The latter salt is a very soluble one; the first, however, is only slightly soluble, so that after a short time it is deposited in colourless or greenish crystals. Ferrous sulphite is also produced by passing sulphur dioxide into a suspension of freshly precipitated ferrous sulphide.[1] The sulphide is dissolved and the sulphite separates out:

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[1] Arbeiter, *Chem. Zentr.*, 1913, i, 1933.

[2] Rodt, *Zeit. angew. Chem.*, 1916, **29**, i, 422.

[3] Glatzel, *Ber.*, 1890, **23**, 37.

[4] Allen, *J. Washington Acad. Sci.*, 1911, **1**, 170.

[5] Benedek, *Zeit. Kryst. Min.*, 1910, **48**, 447; Plummer, *J. Amer. Chem. Soc.*, 1911, **33**, 1487.

$$FeS + SO_2 + H_2O = FeSO_3 + H_2S.$$

A solution of ferrous sulphite becomes red on exposure to the air owing to oxidation.[2]

Ferric hydroxide dissolves in sulphurous acid to give a yellow solution which probably contains ferric sulphite, but this compound has not been isolated. The solution rapidly changes colour from yellow to green, owing to reduction of the ferric sulphite to ferrous sulphite and dithionate.[3]

$$Fe_2(SO_3)_3 = FeSO_3 + FeS_2O_6.$$

Ferrous Sulphate, or *Green Vitriol*, $FeSO_4,7H_2O$, was probably used by Geber. Agricola, in his discourse *De Re Metallica*, mentions two kinds of pyrites. The one, such as coal-brasses, decomposes spontaneously and yields a vitriol; whilst the other, as the ordinary Mason's pyrites, does so only when it is roasted. Its preparation by dissolving iron in sulphuric acid was described by "Basil Valentine" in his *Treatise on Natural and Supernatural Things*: "Take oleum vitrioli; dissolve therein *mars*, and prepare a vitriol from it." In his last volume he describes the method for preparing sulphide of iron and for obtaining vitriol from it: "*Limaturam ferri* and *sulphur and* calcined in a potter's furnace until it becomes tinted purple; then pour upon this distilled water, when a fine green liquid is formed. Draw this off *ad tertias*, allow it to deposit, and thus obtain an artificial vitriol." Green vitriol occurs as the mineral melanterite, either crystalline or in fibrous stalactitic forms, but generally massive and pulverulent. It is usually derived from the decomposition of pyrites or marcasite. Ferrous sulphate is likewise frequently found in solution in drainage water from mines, and it is manufactured on a large scale from this source. Large quantities of green vitriol (about 100 tons per week) are manufactured in South Lancashire from the pyrites occurring in the coal measures. These are piled up in heaps and exposed to the atmosphere. The soluble ferrous sulphate, together with the excess of sulphuric acid formed, runs into underground tanks, where the excess of acid is removed by means of scrap iron. On evaporating the liquor large crystals of ferrous sulphate are obtained. Ferrous sulphate is formed also as a by-product in the manufacture of copper sulphate or blue vitriol (p. 449). The commercial salt not infrequently contains traces of copper sulphate, and this may be detected and separated, as was pointed out by Vigani, so long ago as 1683, by leaving the solution in contact with metallic iron until the whole of the copper is precipitated. Another common impurity is ferric sulphate; this may be removed by recrystallisation, but zinc sulphate, manganese sulphate, and other salts cannot thus be got rid of. Hence when chemically pure ferrous sulphate is needed it is best to treat an excess of iron wire with dilute sulphuric acid. When the evolution of hydrogen has ceased, the liquid is boiled together with the undissolved portion of the wire, filtered, and crystallised.

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[1] Henderson and Weiser, *J. Amer. Chem. Soc.*, 1913, **35**, 239.

[2] Seubert and Elten, *Zeit. anorg. Chem.*, 1893, **4**, 44.

[3] Carpenter, *Journ. Chem. Soc.*, 1902, **81**, 1.

Ferrous sulphate forms well-defined monoclinic crystals with a specific gravity of 1·889 at 4° (Joule and Playfair), but is dimorphous, often crystallising in rhombic prisms, which are isomorphous with zinc sulphate. These are obtained when a crystal of zinc sulphate is thrown into a supersaturated solution of the ferrous salt, but, on the other hand, if a crystal of copper sulphate be employed, triclinic crystals are obtained having the composition $FeSO_4,5H_2O$ and isomorphous with copper sulphate (Lecoq de Boisbaudran). When ferrous sulphate is heated in a vacuum to 140°, it yields a white powder of the monohydrate, $FeSO_4,H_2O$, and this, when gently heated in absence of air, yields the anhydrous salt, $FeSO_4$. Exposed to the air, the commercial heptahydrate gradually loses water and becomes converted into basic ferric sulphate, but the pure dry salt is quite stable and does not effloresce or oxidise.[1]

Up to 100° there are three hydrates which are successively in stable equilibrium with the aqueous solution, namely, the heptahydrate, stable from −1·82° (the eutectic point) to 56·6°, the tetrahydrate, from 56·6° to 64·4°, and the monohydrate, above the latter temperature.[2] The solubility at various temperatures, in grams of anhydrous ferrous sulphate per 100 grams of saturated solution, is as follows:

0°	10°	20°	40°	54°	64°	77°	90°
13·5	17·0	21·0	28·7	34·3	35·7	31·5	27·2.

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[1] De Forcrand, *Compt. rend.*, 1914, **158**, 20.

[2] Fränckel, *Zeit. anorg. Chem.*, 1907, **55**, 223.

In addition to those already mentioned, hydrates with $6H_2O$, $3H_2O$, and $2H_2O$ have been described.

Ferrous sulphate is insoluble in concentrated sulphuric acid and absolute alcohol, and the addition of strong sulphuric acid to a saturated solution of the salt causes the precipitation of the monohydrate.[1] A solution of ferrous sulphate, like the chloride, absorbs nitric oxide. The dark brown saturated solution, which probably contains the compound $FeSO_4,NO$ (p. 1293), gives off the gas in a vacuum as well as when heated; in the latter case small quantities of nitrogen monoxide and ferric sulphate are formed. When the brown solution is mixed with strong sulphuric acid, keeping the mixture cool, it becomes purple-red; upon this reaction the well-known test for nitric acid and the nitrates depends, as well as the method of detecting the presence of nitrous fumes in sulphuric acid.

By treating a concentrated solution of ferrous sulphate with chlorine and allowing to evaporate the substance $FeSO_4Cl,6H_2O$ is obtained. It may also be prepared by heating a mixture of ferric chloride and ferric sulphate.[2]

Ferrous sulphate solution is readily oxidised by oxygen or air, and the rate of oxidation is proportional to the partial pressure of the oxygen.[3] The presence of inert salts reduces the rate owing to the decreased solubility of oxygen in the solution.[4] Potassium permanganate and dichromate also readily oxidise ferrous sulphate solution, and titration with solutions of these salts affords a rapid and convenient method of estimating iron. The reducing power of ferrous sulphate is utilised in photography, where, in the process of "toning" ferrous sulphate is used to precipitate gold from gold chloride.

$$AuCl_3 + 3FeSO_4 = FeCl_3 + Fe_2(SO_4)_3 + Au.$$

Green vitriol is largely used in the arts and manufactures for the preparation of iron mordants, inks, Prussian blue, etc.

Ferrous sulphate enters into the composition of various double salts. There are, for instance, the red and yellow substances formed when sulphuric acid acts on a concentrated mixed solution of ferrous sulphate and copper sulphate.[5] Again, ferrous sulphate, like the sulphates of the metals of the magnesium group, copper, and manganese, forms crystalline double salts, with the sulphates of the alkali-metals; of these the following is the most important.

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[1] Compare Kenrick, *J. Physical Chem.*, 1908, **12**, 693; Wirth, *Zeit. anorg. Chem.*, 1913, **79**, 360; Florentin, *Bull. Soc. chim.*, 1913, [4], **13**, 362.

[2] Röhm, *Collegium*, 1921, **614**, 282.

[3] Ennos, *Proc. Camb. Phil. Soc.*, 1913, **17**, 182.

[4] MacArthur, *J. Physical Chem.*, 1916, **20**, 545.

[5] Étard, *Compt. rend.*, 1878, **87**, 602; Scott, *Journ. Chem. Soc.*, 1897, **71**, 564; Allmand, *Zeit. anorg. Chem.*, 1909, **61**, 202.

Ferrous Ammonium Sulphate or *Mohr's Salt*,

$$FeSO_4,(NH_4)_2SO_4,6H_2O,$$

is obtained when the calculated quantities of ammonium sulphate and green vitriol are dissolved in the minimum quantity of hot water, and the filtered solution is allowed to crystallise or is precipitated with alcohol. It forms clear, hard, bluish-green, monoclinic crystals, which have a specific gravity of 1·813. One hundred parts of water dissolve (Tobler):

At	0°	20°	30°	60°	75°
$FeSO_4,(NH_4)_2SO_4$	12·2	21·6	28·1	44·6	56·7.

This salt is a very stable one, and does not readily undergo alteration in the air, being much less easily oxidised than green vitriol itself. Hence it is largely used instead of the latter salt for the purposes of volumetric analysis. The double sulphates of ferrous sulphate with those of the alkali metals are prepared in a similar manner and are all isomorphous.[1]

Ferrous Disulphate, FeS_2O_7, separates out as a white powder when a concentrated solution of ferrous sulphate is mixed with several times its volume of concentrated sulphuric acid. It forms microscopic prisms, and is decomposed by water into sulphuric acid and green vitriol.[2]

Ferric Sulphate, $Fe_2(SO_4)_3$, is obtained by the action of nitric acid on a hot solution of green vitriol to which the requisite quantity of sulphuric acid has been added:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

The yellowish-brown solution gives a syrupy liquid when concentrated, from which colourless crystals are deposited on standing. When these are heated, or when sulphuric acid is added to the concentrated solution, the anhydrous salt is formed as a white powder, which dissolves slowly in water, whilst by the action of green vitriol on boiling sulphuric acid the same salt is deposited in small, crystalline scales or rhombic prisms:

$$2FeSO_4 + 2H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + 2H_2O.$$

Various hydrates also have been described.[3]

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[1] Tutton, *Proc. Roy. Soc.*, 1913, [*A*], 88, 361.

[2] Bolas, *Journ. Chem. Soc.*, 1874, 27, 212.

[3] Recoura, *Compt. rend.*, 1905, 141, 106; 1907, 144, 1427.

When a dilute solution of ferric sulphate is boiled or incompletely precipitated with alkalis, or when a solution of green vitriol is allowed to oxidise in the air, various basic ferric sulphates are formed.[1] An iron mordant obtained by oxidising green vitriol with nitric acid deposits on standing large, transparent crystals, which are probably monoclinic, having the composition $FeSO_4(OH),7H_2O$; these are decomposed by water with formation of the insoluble salt, $Fe_2SO_4(OH)_4,5H_2O$.[2] Various other basic ferric sulphates occur as minerals,[3] being formed by the oxidation of the sulphides of iron. Amongst these may be mentioned vitriol ochre, $FeSO_4(OH)_4,2Fe(OH)_3,H_2O$. This frequently occurs in long, brown, green, or ochreous yellow stalactites; whilst copiapite, $Fe_2(SO_4)_3Fe_2(SO_4)_2(OH)_2,10H_2O$, occurs in sulphur-yellow tablets or crystalline scales, and fibro-ferrite, $2Fe_2(SO_4)_2(OH)_2,Fe_2SO_4(OH)_4,24H_2O$, forms a pale yellow or nearly white pearly or silky mass.

Anhydrous ferric sulphate, when heated, dissociates into ferric oxide and sulphur trioxide. This fact is of importance in connection with the use of ferric oxide as a catalyst in the contact process of manufacturing sulphuric acid.[4]

Ferroso-ferric Sulphates.—The two sulphates of iron form various double salts, of which some are found in the mineral kingdom. Amongst these is roemerite, $Fe_3(SO_4)_4,12H_2O$, yellow, monoclinic crystals, occurring at the Rammelsberg mine, near Goslar, with another similar mineral termed voltaite, in which a part of the iron is replaced by isomorphous metals.

Ferric Potassium Sulphate, $Fe_2(SO_4)_3,K_2SO_4,24H_2O$, or *Iron Alum*, is obtained when the proper quantity of potassium sulphate is added to a solution of ferric sulphate and the concentrated solution allowed to stand for some days about 0°. The salt forms bright violet octahedra, and dissolves in about five parts of cold water. If caustic potash is added to the solution and the dark liquid allowed to evaporate, transparent, yellowish-brown, hexagonal crystals separate out which have the composition $5K_2SO_4,2Fe_2(SO_4)_2(OH)_2,16H_2O$, and possess the peculiar optical properties of tourmaline. This salt easily decomposes into iron alum and an insoluble basic ferric salt.

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[1] Compare Cameron and Robinson, *J. Physical Chem.*, 1907, **11**, 641; Applebey and Wilkes, *Journ. Chem. Soc.* 1921, **121**, 337; Posnjak and Merwin, *J. Amer. Chem. Soc.*, 1922, **44**, 1965.

[2] *Ber.*, 1875, **8**, 771.

[3] See Scharizer, *Zeit. Kryst. Min.*, 1907, **43**, 113; 1909, **46**, 427; 1913, **52**, 372; Wirth and Bakke, *Zeit. anorg. Chem.*, 1914, **87**, 13.

[4] Keppeler and D'Ans, *Zeit. physikal. Chem.*, 1908, **62**, 89; Wöhler, Plüddemann, and Wöhler, *Ber.*, 1908, **41**, 703; *ibid.*, 1908, **62**, 641; Bodenstein and Suzuki, *Zeit. Elektrochem.*, 1910, **16**, 912.

Ferric Ammonium Alum, $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, closely resembles the potassium derivative, and is sometimes termed "iron alum." It is hydrolysed in solution, a basic iron sulphate, $2Fe_2O_3,SO_3$, being precipitated.[1] Several other double salts of ferric and ammonium sulphates have been described.[2]

IRON AND THE ELEMENTS OF THE NITROGEN GROUP.

566 *Iron Nitrides*.—When nitrogen is passed over heated iron, the metal is rendered brittle, probably owing to the alternate formation and decomposition of an iron nitride, but the latter compound cannot be prepared in this manner.[3] The nitride may, however, be obtained by heating the metal in ammonia, as shown by Berthelot and confirmed by Stahlschmidt.[4]

If ammonia in excess is allowed to act on anhydrous ferrous chloride or bromide, or on finely divided reduced iron, or on iron amalgam at a temperature of about 420°, iron nitride is obtained as a dull grey powder.[5] In the compact state, it is best obtained by heating iron wire or rod to a bright red heat with a large excess of ammonia, excess being necessary inasmuch as the hydrogen formed reduces iron nitride at the same temperature as that at which it is produced.[6]

The substance has a composition corresponding with the empirical formula Fe_2N, and is so brittle that it may be readily powdered in a mortar; it is somewhat magnetic, and has a specific gravity of 6·0–6·5. It begins to evolve nitrogen at 500° and the decomposition is rapid at 600°.[7] It readily oxidises when heated in the air, and ignites when warmed in chlorine. It is dissolved by dilute hydrochloric and sulphuric acids with evolution of hydrogen, and formation of ferrous and ammonium salts.

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[1] See Rae, *Journ. Chem. Soc.*, 1916, **109**, 1331.

[2] Lachoud and Lepierre, *Compt. rend.*, 1892, **114**, 915.

[3] See Maxted, *J. Soc. Chem. Ind.*, 1918, **37**, 105.

[4] *Pogg. Ann.*, 1865, **125**, 37.

[5] Fowler, *Journ. Chem. Soc.*, 1901, **79**, 285; White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1343; Girardet, *Bull. Soc. chim.*, 1910, **7**, 1028. Charpy and Bonnerot, *Compt. rend.*, 1914, **158**, 944; Noyes and Smith, *J. Amer. Chem. Soc.*, 1921, **43**, 475.

[6] Beilby and Henderson, *Journ. Chem. Soc.*, 1901, **79**, 1249.

[7] Maxted, *loc. cit.*; Charpy and Bonnerot, *loc. cit.*

According to Guntz,[1] *ferrous nitride*, Fe_3N_2, and *ferric nitride*, FeN, both of which are black powders and differ from the foregoing, are formed by heating lithium nitride with ferrous potassium chloride and ferric potassium chloride respectively. A substance of the formula Fe_5N_2 was found by Silvestri[2] as a lustrous, metallic deposit on the Etna lavas. This may be a mixture or solid solution of iron and the nitride, Fe_2N.

Ferrous Nitrate, $Fe(NO_3)_2,6H_2O$, is best obtained by the decomposition of green vitriol with barium nitrate, the filtrate being evaporated in a vacuum over sulphuric acid. It is very soluble in water and very unstable, easily passing into ferric nitrate. When iron is dissolved in cold dilute nitric acid, the following reaction takes place (Berzelius):

$$8Fe + 20HNO_3 = 8Fe(NO_3)_2 + 2NH_4NO_3 + 6H_2O,$$

but the reaction varies greatly with the concentration of the acid and the temperature.[3]

Ferric Nitrate, $Fe(NO_3)_3$, is formed by dissolving iron in nitric acid. The brown concentrated solution deposits, on addition of nitric acid, according to the acidity and the concentration of the solution, colourless cubes of $Fe(NO_3)_3,6H_2O$, or colourless, monoclinic crystals containing 9 molecules of water.[4] These are very deliquescent, and dissolve in water, forming a brown liquid, which becomes colourless when concentrated nitric acid is added to it. Ferric nitrate is used as a mordant in dyeing and calico printing.

Several basic ferric nitrates, soluble and insoluble, are known.

Nitroso-compounds of Iron.—As already mentioned, nitric oxide is readily absorbed by solutions of ferrous salts with formation of dark olive-green to black solutions, which contain unstable compounds of nitric oxide with the ferrous salt. The maximum absorption for solutions of ferrous salts in water, alcohol, and other neutral solvents is found to be in the proportion of 1 mol. NO to 1 mol. ferrous salt. The reaction, however, is reversible, the degree of dissociation not only varying with different ferrous salts, but being dependent also on the pressure, the temperature, the concentration of ferrous salt, the solvent, and the presence of other dissolved substances.[5] When dissolved in strong hydrochloric acid, ferrous chloride absorbs about twice as much nitric oxide as when dissolved in the same quantity of water.[1]

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[1] *Compt. rend.*, 1902, **135**, 738.

[2] *Pogg. Ann.*, 1870, **157**, 165.

[3] Montemartini, *Journ. Chem. Soc.*, 1892, **62**, 1278.

[4] See Cameron and Robinson, *J. Physical Chem.*, 1909, **13**, 251.

[5] Manchot and Zechentmayer, *Annalen*, 1906, **350**, 368; Manchot and Hüttner, *ibid.*, 1910, **372**, 153.

Anhydrous ferric chloride also absorbs nitric oxide, forming the compounds $2FeCl_3,NO$ and $4FeCl_3,NO$, which are reddish-brown, non-crystalline, hygroscopic powders. When nitric oxide is passed into an ethereal solution of ferric chloride, nitrosyl chloride is formed, and on evaporation over sulphuric acid, black needles of the composition $FeCl_2,NO,2H_2O$ are obtained, whilst at 60° the anhydrous compound, $FeCl_2,NO$, is formed crystallising in yellow needles.[2]

In addition to the foregoing unstable nitroso-derivatives others of a more stable nature have been prepared. These were discovered by Roussin,[3] who prepared them by the action of ferrous sulphate on mixed solutions of the nitrites and sulphides of the alkalis, and they have since been investigated by many other chemists.[4] Their exact constitution has not yet been determined, but they are closely allied to the ferrocyanides and similar compounds, and consist of salts of complex acids containing both the iron and nitroso-groups in the acid radical. Two classes of salts have been prepared, viz., the *ferrodinitroso*-derivatives, such as the salt $K[Fe(NO)_2S]$, and the *ferroheptanitroso*-derivatives, such as the salt $K[Fe_4(NO)_7S_3]$.

Potassium Ferrodinitrososulphide, $K[Fe(NO)_2S],2H_2O$, is obtained by the action of potash on the heptanitrososulphide.[5] It forms dark red crystals, insoluble in water, and decomposes violently when heated, yielding, among other products, potassium and ammonium sulphates. By the action of sulphuric acid, it yields the free *acid*, $H[Fe(NO)_2S]$, which slowly decomposes in the cold into sulphuretted hydrogen, nitrogen, nitrous oxide, and the heptanitroso-acid.

The corresponding salts of the other alkalis,[6] and in addition the crystalline *ethyl* and *phenyl* derivatives, $C_2H_5[Fe(NO)_2S]$ and $C_6H_5[Fe(NO)_2S]$, are known.

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[1] Kohlschütter and Kutscheroff, *Ber.*, 1907, **40**, 873.

[2] Thomas, *Compt. rend.*, 1895, **120**, 447.

[3] Roussin, *ibid.*, 1858, **46**, 224.

[4] Porczinsky, *Annalen*, 1863, **125**, 302; Rosenberg, *Ber.*, 1870, **3**, 312; Pavel, *ibid.*, 1882, **15**, 2600; Marchlewski and Sachs, *Zeit. anorg. Chem.*, 1892, **2**, 175; Hofmann and Wiede, *ibid.*, 1895, **8**, 318; 1895, **9**, 295; 1896, **11**, 281; Marié and Marquis, *Compt. rend.*, 1896, **122**, 137.

[5] Pavel, *Ber.*, 1882, **15**, 2600; Rosenberg, *Arkiv Kem. Min. Geol.*, 1911, **4**, [3] 1.

[6] Roussin, *Compt. rend.*, 1858, **46**, 224.

Potassium Ferrodinitrosothiosulphate, $K[Fe(NO)_2S_2O_3],H_2O$, is made by passing nitric oxide into a strong solution of potassium thiosulphate and ferrous sulphate. On concentration, the salt is obtained as reddish-brown crystals which are sparingly soluble in cold water. The corresponding salts of the other alkalis and of ammonium are prepared in a similar manner.[1]

Potassium Ferroheptanitrososulphide, $K[Fe_4(NO)_7S_3],H_2O$, is the most stable of these salts, and is obtained by adding a solution of ferrous sulphate to one of potassium nitrite and sulphide.[2] It is formed also by boiling a solution of the ferrodinitrosothiosulphate, sulphur dioxide being evolved and ferric hydroxide precipitated.[1] It forms dark, monoclinic crystals with a diamond lustre, and is only sparingly soluble in water. Dilute sulphuric acid precipitates from its solution the free *ferroheptanitrososulphhydric acid* as an amorphous, brown mass, but when the salt is heated with concentrated sulphuric acid it yields nitric oxide, nitrogen, sulphuretted hydrogen, sulphur, and ferric ammonium and potassium sulphates.

The corresponding salts of the other alkalis and of the alkaline earths have been obtained and also the *thallium* salt. The *ammonium* salt is formed by the action of nitric oxide on freshly precipitated ferrous sulphide suspended in water, part of the nitric oxide being reduced to ammonia,[3] or by double decomposition of the sodium salt with ammonium carbonate. The *ferrous* salt, $Fe[Fe_4(NO)_7S_3]_2$, is likewise prepared by double decomposition of the sodium salt with ferrous sulphate.

567 *Phosphides of Iron.*—In the year 1780, J. C. F. Meyer, while examining the cause of the cold-shortness of iron, came to the conclusion that this was produced by the presence of a peculiar metal, to which he gave the name *hydrosiderum*. The subject was investigated shortly afterwards by Bergman, who found that when the residue obtained by dissolving cold-short iron in sulphuric acid is fused before the blowpipe with reducing agents, a metallic bead is obtained which he also believed to be a peculiar metal; to this he gave the name of *siderum*. In 1784, Meyer repeated his experiments and decided that the substance thus obtained was a compound of iron and phosphoric acid; later it was identified as a phosphide of iron.

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[1] Hofmann and Wiede, *Zeit. anorg. Chem.*, 1895, **8**, 318; **9**, 295.

[2] Pavel, *Ber.*, 1879, **12**, 1407.

[3] Hofmann and Wiede, *loc. cit.* See also *Atti R. Accad. Lincei*, [5], 1906, **15**, ii., 467; 1907, **16**, i., 664; ii., 542, 584, 658, 740; 1908, **17**, i., 202, 424, 545.

One phosphide of iron, Fe_2P, is obtained as a porous, non-magnetic powder by fusing ferrous or ferric phosphate with lamp-black under a layer of sodium chloride; and in lustrous, grey crystals by fusing cuprous phosphide with 10 parts of iron filings in the electric furnace.[1] When heated in the air, it is converted into a basic phosphate, $2Fe_2O_3,P_2O_5$.

The phosphide, Fe_3P, is obtained from fused mixtures of phosphorus and iron containing more than 84·4 per cent. of iron, and is prepared also by fusing copper phosphide with a sufficient quantity of iron, when the compound Fe_3P, in an almost pure state, rises to the top as a separate phase.[2] It has been found as small, tin-white crystals in iron from a blast furnace.[3] This phosphide dissolves in concentrated hydrochloric acid, giving ferrous chloride, phosphoric acid, and pure hydrogen.

When iron pyrites or iron powder is ignited in a stream of phosphine, a grey, non-magnetic powder, having the composition Fe_3P_4, is obtained, whilst the compound FeP is left as a dark-grey powder when the monosulphide is ignited in the same gas, or when iron is heated in phosphorus vapour. The compound Fe_2P_3 is produced by strongly heating phosphorus and ferric chloride placed in separate boats in a tube in a current of carbon dioxide, and forms hard, metallic, non-magnetic crystals.[4]

When obtained in distinct crystals, these phosphides of iron are mostly insoluble in single acids, but dissolve in a mixture of nitric and hydrofluoric acids, whilst in the loose porous state they are attacked by hot hydrochloric acid with evolution of phosphine and formation of phosphoric acid. They do not undergo alteration in the air, and can be fused in all proportions with metallic iron. Many other iron phosphides which have been described, and possibly some of the above, are probably in reality mixtures of a true phosphide and iron.[5]

Ferrous Phosphate, $Fe_3(PO_4)_2,8H_2O$, occurs as the mineral vivianite, crystallising in monoclinic prisms. In its pure state it is colourless, but it generally possesses a green or blue tint, owing to partial oxidation. It is found also as an earthy mass termed blue iron earth, sometimes dispersed through clay, and together with bog iron ore, and in the cavities in fossil bones. When a solution of green vitriol is precipitated with sodium phosphate, a white precipitate is obtained, which, however, soon becomes blue or green on exposure to air. If the liquid and the precipitate are allowed to stand together for a week at a temperature of 60–80°, the compound is converted into small crystals which become blue on exposure to the air (Debray). The precipitated phosphate is used in medicine.

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[1] Maronneau, *Compt. rend.*, 1900, **130**, 656.

[2] Le Chatelier and Wologdine, *ibid.*, 1909, **149**, 709. Compare Stead, *J. Iron Steel Inst.*, 1900, **58**, 60; Saklatwalla, *ibid.*, 1908, **77**, 92; Gercke, *Metallurgie*, 1908, **5**, 604; Konstantinoff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1220.

[3] Spencer, *Min. Mag.*, 1916, **17**, 340.

[4] Granger, *Compt. rend.*, 1896, **122**, 936.

[5] See Le Chatelier and Wologdine, *loc. cit.*; Khun, *Chem. Zeit.*, 1910, **34**, 45.

The monacid salt, $FeHPO_4,H_2O$, is prepared by dissolving iron in phosphoric acid solution. An interesting derivative has been prepared by Manchot.[1] When ammonium phosphate solution is added to a solution of ferrous chloride in alcohol saturated with nitric oxide, a dark brown, viscid oil is precipitated. This may be solidified by placing in a freezing mixture, and on recrystallisation at low temperatures yields brown, flaky crystals having the composition $FeHPO_4,NO$ and melting at 16°. On exposure to air, the substance is slowly oxidised to ferric phosphate.

When iron is dissolved in excess of phosphoric acid, colourless needles of the diacid salt, $Fe(H_2PO_4)_2,2H_2O$, are deposited after some time, and these alter rapidly on exposure to air.[2]

Ferric Phosphates.—The *normal orthophosphate*, $FePO_4,2H_2O$, is obtained as a yellowish-white precipitate by adding ordinary sodium phosphate to normal ferric chloride. It is soluble in dilute mineral acids, but not in cold acetic acid, and is slowly decomposed by water. When ferric hydroxide is dissolved in orthophosphoric acid and the solution rapidly evaporated, the *diacid salt*, $Fe(H_2PO_4)_3$, is obtained as a pink, crystalline powder, which decomposes in moist air and deposits crystals of the *monacid salt*, $2FeH_3(PO_4)_2,5H_2O$ (Erlenmeyer). *Ferric metaphosphate*, $Fe(PO_3)_3$, is deposited in pink plates when ferric hydroxide is digested with glacial phosphoric acid at 100°.[3] Ferric phosphate has been obtained in the colloid state.[4]

Basic iron phosphates occur in nature, and frequently form a constituent of limonite. Ferric phosphate also occurs as dufrenite, $Fe_2(OH)_3PO_4$, which is found sometimes in rhombic crystals, but more generally in needles or as a radiated, fibrous mass. Vivianite is often oxidised and is converted into beraunite,

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[1] *Ber.*, 1914, **47**, 1601.

[2] Erlenmeyer, *Annalen*, 1878, **194**, 182.

[3] Hautefeuille and Margotte, *Compt. rend.*, 1888, **106**, 135. See also Johnsson, *Ber.*, 1889, **22**, 976.

[4] Holmes and Rindfusz, *J. Amer. Chem. Soc.*, 1916, **38**, 1970.

$Fe(PO_4),2Fe_2PO_4(OH)_3,4H_2O$, occurring in small, foliated aggregates having a hyacinth-red colour.

568 *Arsenides of Iron.*—When metallic iron is ignited with an excess of arsenic in the absence of air, a white and very brittle mass of FeAs is obtained. The arsenide $FeAs_2$ occurs as the mineral löllingite in silver-white, rhombic prisms. It is obtained artificially by heating finely powdered iron with the vapour of arsenic under pressure.[1] This artificial product, heated in a current of hydrogen, yields the arsenide FeAs as a silver-white, crystalline powder. The study of the freezing points of alloys of iron and arsenic indicates the existence of other arsenides, viz.:—Fe_3As_2, Fe_2As, and Fe_5As_4.[2] Mispickel or arsenical pyrites, FeAsS, crystallises in short, rhombic prisms of a silver-white colour; a portion of the iron is frequently replaced by cobalt, and this mineral serves as the chief source of arsenic compounds.

Ferric Arsenite.—$Fe_4O_5(OH)_5As[=4Fe_2O_3,As_2O_3,5H_2O]$. This basic salt is a voluminous, brown precipitate closely resembling ferric hydroxide, and is obtained by adding an aqueous solution of arsenious oxide, or an arsenite, to ferric acetate.

Ferric Arsenates.—The normal arsenate occurs as scorodite, $Fe(AsO_4),2H_2O$, in brown, rhombic, vitreous crystals. Basic arsenates are also found in the mineral kingdom; amongst these we have iron-sinter or pharmacosiderite, $3FeAsO_4,Fe(OH)_3,6H_2O$, which occurs crystallised in the regular system in green or brownish-green, adamantine crystals. The acid arsenate, $2Fe_2(HAsO_4)_3,9H_2O$, is a white precipitate obtained by adding hydrogen disodium arsenate to a solution of ferric chloride. It is easily soluble in hydrochloric acid, and separates on evaporation as a white powder. Colloidal ferric arsenate has been prepared both as sol and gel.[3]

IRON AND BORON.

569 *Borides of Iron.*—The compound FeB is formed when the vapour of boron chloride is passed over iron at a dull red heat, or when soft iron is heated with boron in the electric furnace. It is thus obtained as an amorphous powder, or in yellowish-grey crystals of specific gravity 7·15.[4] Other borides, viz., Fe_5B_2,

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[1] Hilpert and Dieckmann, *Ber.*, 1911, **44**, 2378.

[2] Friedrich, *Metallurgie*, 1907, **4**, 129.

[3] Holmes and Rindfusz, *J. Amer. Chem. Soc.*, 1916, **38**, 1970.

[4] Moissan, *Compt. rend.*, 1895, **120**, 173. Compare *ibid.*, 1894, **119**, 1172.

Fe_2B, and FeB_2, have been prepared by heating reduced iron and boron in a porcelain tube in a current of hydrogen or in the electric furnace.[1] These borides of iron are oxidised by moist air, and are dissolved by hot concentrated acids.

IRON AND CARBON.

570 *Iron Carbide* or *triferro carbide*, Fe_3C, occurs in steel (p. 1262) and is known as cementite. It is also found associated with the carbides of cobalt and nickel in meteorites as cohenite. It is formed by heating together iron and carbon, and can be isolated by dissolving the excess of iron in dilute acid.[2] It is a dark grey substance of specific gravity 7·4 and is very brittle. It dissolves slowly in hydrochloric acid, hydrogen and hydrocarbons being evolved. It is also soluble in nitric acid, giving a brown solution. Comparison of the colour of such a solution produced from a given sample of steel with that obtained from a steel of known composition affords a ready method of estimating the amount of cementite in the sample. Iron carbide when moist readily oxidises on exposure to air, and when heated burns, yielding the oxide.

Diferro Carbide, Fe_2C.—By heating together iron and carbon at a definite temperature, suddenly chilling the mass and estimating the combined carbon in the product, Ruff and Goecke[3] showed that the amount of carbon which enters into combination with iron increases with temperature to a well defined maximum at 2220°, when the composition of the iron–carbon compound corresponds to Fe_2C. The diminished solubility of graphite in iron above 2220° is due to dissociation of this carbide into iron and carbon. Below 2220° it dissociates into cementite and carbon, while below 1837° the cementite further dissociates into iron and carbon.[4]

Iron Dicarbide, FeC_2, is obtained as a pale yellow substance by heating iron with carbon and then cooling.[5] It is also formed as a black, magnetic powder by igniting ammonium ferrocyanide or the double compound $(NH_4)_4FeCy_6,2NH_4Cl,3H_2O$. On heating in air, it yields ferric oxide without any change in weight.[1]

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[1] Jassonneix, *Compt. rend.*, 1907, **145**, 121; *Eighth Inter. Cong. App. Chem.*, 1912, **2**, 165; Hannesen, *Zeit. anorg. Chem.*, 1914, **89**, 257; Tschischevsky and Herdt, *Rev. Soc. russe. Met.*, 1915, **1**, 533. Compare Hoffmann, *Chem. Zeit.*, 1910, **34**, 1349.

[2] Moissan, *Compt. rend.*, 1897, **124**, 716; Ruff and Gersten, *Ber.*, 1912, **45**, 63. See also Hilpert and Dieckmann, *ibid.*, 1915, **48**, 1281.

[3] *Metallurgie*, 1911, **8**, 417.

[4] Ruff, *ibid.*, 456. See also Runge, *Zeit. anorg. Chem.*, 1921, **115**, 293; Honda and Murakami, *Sci. Rep. Tohoku Imp. Univ.*, 1921, **10**, 273; *ibid.*, **11**, 119.

[5] Wittorf, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1613.

Other carbides of iron have also been described.[2]

Ferrous Carbonate, $FeCO_3$, occurs naturally as spathic iron ore, which, however, contains larger or smaller quantities of the carbonates of calcium, manganese and magnesium. The mineral is obtained artificially in microscopic rhombohedra by precipitating a solution of green vitriol with sodium bicarbonate and heating the mixture for twelve to thirty-six hours at a temperature of 150° (Sénarmont). When a cold solution of pure ferrous sulphate is treated with sodium carbonate, a flocculent, white precipitate is thrown down which rapidly becomes dirty green from absorption of oxygen and evolution of carbon dioxide, and is at last converted wholly into ferric hydroxide. If the precipitate is washed in total absence of air, it may be obtained pure and colourless, but usually it is a greyish powder, readily oxidised on exposure to air. If the moist precipitate is mixed with sugar, it does not undergo such rapid change.

Ferrous bicarbonate exists in many mineral waters, and is formed in solution by the action of carbonic acid on ferrous carbonate. When such a solution is exposed to the air, carbon dioxide is evolved, and ferric hydroxide deposited. A quantitative study of the rate of oxidation of ferrous bicarbonate has shown that the reaction is of the first order.[3]

Ferric Carbonate is not known in the dry state, since the precipitate produced by the addition of a soluble carbonate to a ferric salt rapidly loses carbon dioxide.

Ferropentacarbonyl, $Fe(CO)_5$, was first obtained by Mond, Quincke, and Langer[4] by allowing iron prepared by the reduction of ferrous oxalate to stand in contact with carbonic oxide. It is evolved when the product is heated to 120°, and may be condensed in a receiver placed in a freezing mixture. Dewar and Jones[5] describe it as a viscous, pale yellow liquid, which forms a yellow, crystalline solid at $-20°$, the latter becoming colourless at the temperature of liquid air. It has a specific gravity of 1·46, and boils at 102·5. The vapour decomposes slowly below very stable at the ordinary temperature, but decomposes at 140–150° into iron and carbonic oxide. It dissolves in many organic solvents, forming dark-green solutions which very readily undergo oxidation. Attempts to determine the molecular weight in benzene solution showed that the substance must be a polymeride containing many $Fe(CO)_4$ groups, possibly $[Fe(CO)_4]_{30}$.

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[1] Ljubavin, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 609. See also Hanemann, *Zeit. anorg. Chem.*, 1913, **84**, 1.

[2] Wittorf, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1613.

[3] Just, *Ber.*, 1907, **40**, 3695.

[4] *Journ. Chem. Soc.*, 1891, **59**, 604, 1090.

[5] *Proc. Roy. Soc.*, [*A*], 1905, **76**, 558; 1907, **79**, 66.

IRON AND CYANOGEN.

571 Hydrocyanic acid gives no precipitate with solutions of ferrous salts, and on addition of ammonia a ferrous ammonium ferrocyanide, $(NH_4)_2Fe^{II}Fe^{II}Cy_6$, is formed which rapidly oxidises to the corresponding ferric salt, $NH_4Fe^{III}Fe^{II}Cy_6$.[1] *Ferrous cyanide*, $FeCy_2$, can be prepared, however, by heating hydrogen ferrocyanide at 300° in absence of air, when hydrogen cyanide is evolved and ferrous cyanide left as a pale yellow powder.[1] It is stable in absence of oxygen up to 430°, when it begins to evolve, nitrogen leaving a mixture of iron, carbon, and iron carbide. When warmed in air, it glows, burning to ferric oxide. It is probably an *iso*cyanide, having the structure $Fe(NC)_2$.[2]

572 Our knowledge of the complex compounds of iron and cyanogen commences with the discovery of Prussian blue in 1704 by a colour-maker named Diesbach. In 1752 Macquer observed that when this colour is boiled with caustic potash, oxide of iron remains, whilst a peculiar salt enters into solution which was named phlogisticated alkali, or yellow prussiate of potash. This body was shown to contain iron and prussic acid by Berthollet in 1787. Proust, in 1806, next found that iron remains in combination with prussic acid when the alkali in the yellow prussiate is replaced by other bases; and Ittner in 1809 considered that the compounds of ferric oxide and other bases with prussic acid are double salts. In opposition to this view, Porrett[3] described experiments from which he drew the conclusion that the so-called double prussiates containing iron are simple salts of a compound acid containing ferrous oxide and prussic acid. This he called *ferruretted chyazic acid*, a name based on the fact that it is a compound of carbon, hydrogen, and azote or nitrogen. Gay-Lussac's classical investigation of

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[1] Hofmann, *Annalen*, 1907, **352**, 54.

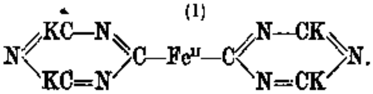
[2] Browning, *Journ. Chem. Soc.*, 1900, **77**, 1234.

[3] *Phil. Trans.*, 1814, 527; *Ann. Phil.*, 1818, **12**, 214; 1819, **14**, 295.

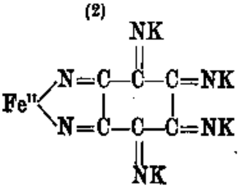
prussic acid followed immediately on Porrett's memoir. In this he proved that the acid is a hydrogen compound of the radicle cyanogen. Berzelius then showed that all the salts of iron and prussic acid may be considered to be double cyanides, and that (according to our present nomenclature) the prussiate of potash is a cyanide of iron and potassium, $Fe(CN)_2,4KCN$. Three years later Gmelin,[1] by acting upon this salt with chlorine, obtained a new compound which, from its colour, was termed red prussiate of potash. This may be regarded as the ferric double salt, $Fe(CN)_3,3KCN$. Gmelin likewise proved that the potassium in the salt may be replaced by hydrogen, thus giving rise to ferricyanic acid. In the following year Gay-Lussac pointed out that the yellow prussiate may be supposed to contain a compound radicle consisting of iron and cyanogen, to which he gave the name *cyanoferre.* Liebig extended this explanation to the other cyanogen compounds containing iron, and considered the above salts as compounds of two isomeric radicles, FeC_6N_6, to which he gave the names of *ferrocyanogen* and *ferricyanogen.*

Many suggestions have been made as to the constitution of these two radicles. Graham[2] and Erlenmeyer[3] assumed these compounds to contain the radicle C_3N_3, on which supposition potassium ferrocyanide would have the constitutional formula (1), whilst Friedel[4] suggested the formula (2), Browning[5] that given under (3), Denigès[6] has proposed (4) and Friend[7] (5), in which the iron atom can be linked to the nitrogen atoms in the 1 : 2, 1 : 3, or 1 : 4 positions.

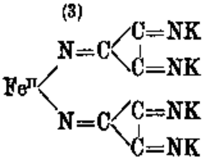
(1)



(2)



(3)



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[1] *Schweiggers' Journ.*, 1822, **34**, 325.

[2] *Elements of Chemistry*, 1850, i, 200.

[3] *Lehrbuch Org. Chem.*, 1867, 148.

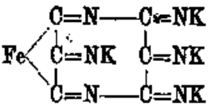
[4] *Compt. rend.*, 1887, **104**, 995.

[5] *Journ. Chem. Soc.*, 1900, **77**, 1238.

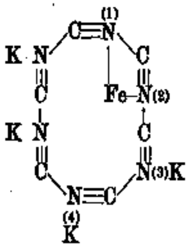
[6] *Bull. Soc. chim.*, 1916, **20**, 79.

[7] *Journ. Chem. Soc.*, 1916, **109**, 715.

(4)



(5)



According to these various hypotheses, the ferrocyanides contain closed chains either of carbon atoms alone, or of carbon and nitrogen atoms. No evidence, however, has been obtained in support of any of these views, and the general properties of the substances are quite distinct from those of the numerous compounds known to contain such closed chains. Moreover, one of the six cyanogen radicles can be replaced by numerous other radicles without any great alteration in general properties, which would not be the case if any of the above formulæ were correct. It is noteworthy that in the methyl ferrocyanides the methyl groups appear to be directly linked to nitrogen, and not to carbon,[1] as would be required by formula (1). Of the other formulæ, only that of Denigès, in which the iron is linked differently from the potassium atoms, offers any explanation of the difference in reactivity of the two metals; and in this case the iron is linked to carbon, whereas, since ferrous cyanide has the *iso*cyanide structure, it should probably be joined to nitrogen. Further, these formulæ admit of the possibility of isomerism which has not yet been found in the case of the inorganic ferrocyanides.

Analogous complex cyanides are formed by other metals of the eighth periodic group, and by metals occupying positions near them in the periodic table, such as chromium, *i.e.*, by those metals which yield complex bases with ammonia, etc., and there is little doubt that these complex bases and the complex cyanides are compounds of the same order. The co-ordination theory of Werner (p. 36), which has thrown much light on the relations of the complex bases, is also of great value in making clear the similar relations of the ferrocyanides and analogous compounds.

According to this hypothesis, the iron atom occupies the centre of the system and is combined with the six cyanogen radicles which are "co-ordinated" with it. The complex radicle thus formed is of an acid nature and is capable of combining with basic elements or groups which form cations in solution. Thus potassium ferrocyanide and ferricyanide are formulated as follows, the co-ordinated group being enclosed in square brackets: for the sake of shortness and simplicity the symbol Cy is used for the cyanogen radicle CN:

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[1] Hartley, *Journ. Chem. Soc.*, 1911, **99**, 1549.

Potassium Ferrocyanide	*Potassium Ferricyanide*
$K_4[Fe^{II}Cy_6]$.	$K_3[Fe^{III}Cy_6]$.

The ferrocyanogen radicle is tetracidic, two of the cyanogen valencies being neutralised by the ferrous iron atom, whilst the ferricyanogen radicle is triacidic, as the ferric iron atom neutralises the valency of three cyanogen groups.

One of the six cyanogen groups may be replaced in both ferro- and ferri-cyanides by a large number of other groups, including CO, NO, NO_2, NH_3, H_2O, SO_3, yielding substances which closely resemble the original salts in general properties. If the replacing group be a monovalent acid radicle, such as NO_2, the valency of the group remains unchanged, whilst a divalent acid radicle increases the valency of the group by one unit, and a neutral substance reduces it by one unit. The nitroso-group and ammonia behave in this connection as neutral substances. Thus, sodium carbonylferrocyanide is $Na_3[Fe^{II}(CO)Cy_5]$; sodium nitrosoferricyanide (nitroprusside), $Na_2[Fe^{III}(NO)Cy_5]$; sodium sulphitoferrocyanide, $Na_5[Fe^{II}(SO_3)Cy_5]$; and sodium nitroferrocyanide, $Na_4[Fe^{II}(NO_2)Cy_5]$.

FERROCYANOGEN COMPOUNDS.

573 Until recent years the ferrocyanides served as the point of departure for the preparation of almost all the other cyanogen compounds, and they are still manufactured on the large scale, although the cyanides specially required for the extraction of gold are at present largely obtained in other ways. At present the sodium, potassium, calcium, and iron ferrocyanides are all prepared in quantity.

The method formerly adopted for the manufacture of potassium ferrocyanide, and now obsolete, consisted in heating crude potashes in a cast iron pan, and adding from time to time a mixture of iron filings and nitrogenous organic matter (horns, feathers, dried blood, etc.). The fused mass was allowed to cool, and then lixiviated with warm water, ferrocyanide being obtained by the evaporation of this aqueous extract.[1]

Ferrocyanides are now obtained as by-products in the coal-gas manufacture and other industries in which coal is subjected to destructive distillation. The unpurified gas usually contains a small quantity of cyanogen compounds, chiefly if not entirely as hydrocyanic acid. When the gas is purified by means of ferric oxide (Vol. I., p. 882), this is partially absorbed, together with the sulphuretted hydrogen, and when the absorbing oxide is completely spent it is frequently found to contain sufficient Prussian blue to repay the cost of extraction.

A common method of obtaining the ferrocyanide from the spent oxide is to treat it with hot milk of lime, which converts the Prussian blue into calcium ferrocyanide; on addition of potassium or ammonium chloride to the filtered extract, the sparingly soluble potassium calcium or ammonium calcium ferrocyanide, CaK_2FeCy_6 or $Ca(NH_4)_2FeCy_6$, separates out, and from this pure potassium or sodium ferrocyanide can readily be prepared.

In recent years the hydrocyanic acid has been extracted at a number of gas works by passing the gas, previous to the dry purification (Vol. I., p. 886), through a suitable apparatus in which it is brought into intimate contact with an alkaline liquid to which an iron salt has been added. The latter is converted into ferrous sulphide by the action of the sulphuretted hydrogen in the crude gas, and this is acted on by the hydrocyanic acid in presence of alkali (*e.g.*, potash) as follows:

$$FeS + 6HCy + 2K_2CO_3 = K_4FeCy_6 + H_2S + 2CO_2 + 2H_2O.$$

The potash may be replaced by sodium carbonate or lime, in which case sodium or calcium ferrocyanide is obtained.

If the gas is treated with a solution of ferrous sulphate previous to the removal of ammonia, the latter supplies the necessary alkali, and the hydrocyanic acid is absorbed and converted partly into ammonium ferrocyanide and partly into insoluble double ferrocyanides of ammonium and iron, the latter being almost the sole product when excess of ferrous sulphate is used. This is filtered and converted into soluble ferrocyanides by boiling with alkalis, the ammonia evolved being recovered as sulphate by absorption in sulphuric acid.

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[1] For full details of this and the modern methods of obtaining ferrocyanides, see the article on "Cyanides" in Thorpe's *Dictionary of Applied Chemistry.*

Ferrocyanides are now prepared also from thiocyanates, the latter being either made synthetically from carbon disulphide or recovered from crude coal-gas (Vol. I., p. 887). The thiocyanate is fused in pots and completely dried by passing through it a current of inert gas, and then heated with dry iron borings free from rust, air being excluded:

$$6NaCyS + 6Fe = 6NaCy + 6FeS.$$

The melt is then treated with water and boiled up with steam in a vat, when sodium ferrocyanide is formed together with sodium sulphide:[1]

$$6NaCy + FeS = Na_4FeCy_6 + Na_2S.$$

Hydrogen Ferrocyanide or *Ferrocyanic Acid*, $H_4Fe^{II}Cy_6$.—This is best obtained when pure hydrochloric acid is added to an equal volume of a cold saturated solution of potassium ferrocyanide. The precipitate which forms is dried on a porous plate in absence of air, then dissolved in alcohol, and precipitated by ether.[2] It is a white powder crystallising in small needles. Larger crystals may be obtained by pouring a layer of ether on to the alcoholic solution. Ferrocyanic acid is easily soluble in water or alcohol. It possesses a strongly acid taste and reaction, and liberates not only acetic, but even oxalic acid, from its salts. It oxidises quickly on exposure to air, especially when warmed, forming hydrocyanic acid and ferric ferrocyanide:

$$7H_4FeCy_6 + O_2 = 24HCy + Fe_4[FeCy_6]_3 + 2H_2O.$$

This reaction is employed in calico-printing, the cloth being printed with a mixture of tartaric acid and yellow prussiate, and then steamed.

When the solution of the acid is boiled, hydrocyanic acid is evolved and a white precipitate of ferrous hydrogen ferrocyanide remains behind:

$$2H_4[Fe^{II}Cy_6] = 6HCy + H_2Fe^{II}[Fe^{II}Cy_6].$$

When heated at 300° in absence of air it decomposes, hydrogen cyanide being evolved and ferrous cyanide formed. Some regard the product as a ferrous ferrocyanide, $Fe^{II}_2(Fe^{II}Cy_6)$, rather than as the simple cyanide.

Ferrocyanic acid gives a series of salts in which it is tetrabasic, and also an ethyl derivative, $(C_2H_5)_4Fe(Cy)_6$.[3] The molecular weight of the latter in aqueous solution is in accordance with the simple formula just given,[1] whereas the calcium and strontium salts exist as double molecules.[2] The acid forms crystalline compounds with ether, ethyl acetate, and other organic esters.[3]

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[1] *J. Soc. Chem. Ind.*, 1895, **14**, 656.

[2] Liebig, *Annalen*, 1853, **87**, 127.

[3] Hartley, *Journ. Chem. Soc.*, 1913, **103**, 1196.

Potassium Ferrocyanide or *Yellow Prussiate of Potash*, $K_4FeCy_6,3H_2O$.—The commercial manufacture of this salt has been described above. It is obtained also when a ferrous salt is added to potassium cyanide; a brown precipitate of uncertain composition is first formed, but quickly dissolves in excess of potassium cyanide, yielding potassium ferrocyanide. The latter is formed also by the action of potassium cyanide solution on metallic iron in absence of air, slowly in the cold and quickly on heating:

$$6KCy + Fe + 2H_2O = K_4FeCy_6 + 2KOH + H_2.$$

Potassium ferrocyanide forms tetragonal pyramids, sp. gr. 1·83, in which the basal faces are usually dominant. They are of a lemon-yellow colour and generally opaque. Small crystals, on the other hand, are amber-coloured and transparent.

Potassium ferrocyanide does not undergo alteration in pure air at the ordinary temperature, but when heated to 60° it begins to lose its water of crystallisation, which is removed completely at 110°, the anhydrous salt remaining as a white powder. It has a sweetish, saline, and somewhat bitter taste, and is not poisonous, acting in large doses as an aperient. One hundred parts of water dissolve about 25 parts of K_4FeCy_6 at 25°, and about 87 parts at 100°, but the solubility is increased by the presence of sodium ferrocyanide. It is insoluble in alcohol even when the latter is considerably diluted with water. When its solution is exposed to light for some time Prussian blue separates out, and on long-continued boiling of the solution in the air ammonia is given off and the liquid becomes alkaline.

By adding very dilute hydrochloric acid gradually to a boiling solution of potassium ferrocyanide, the compound $Fe_2{}^{III}Fe^{II}K_8[FeCy_6]_4,6H_2O$ is precipitated, and the use of ammonium chloride instead of hydrochloric acid gives the compound $Fe_2{}^{III}Fe^{II}(NH_4)_7K[FeCy_6]_4,3H_2O$.[4]

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[1] Buchböck, *Zeit. physikal. Chem.*, 1897, **23**, 157.

[2] Berkeley, Hartley, and Burton, *Phil. Trans.*, 1908, [*A*], **209**, 177; Berkeley, Hartley, and Stephenson, *ibid.*, 319.

[3] Browning, *loc. cit.*; Baeyer and Villiger, *Ber.*, 1901, **34**, 2679.

[4] Williams, *Proc. Chem. Soc.*, 1913, **29**, 54.

On boiling potassium ferrocyanide with dilute sulphuric acid, hydrogen cyanide is evolved and Everitt's salt is produced.[1]

$$2K_4FeCy_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe^{II}[Fe^{II}Cy_6] + 6HCN.$$

Concentrated sulphuric acid reacts with potassium ferrocyanide with evolution of carbon monoxide:

$$K_4FeCy_6 + 8H_2SO_4 + 6H_2O = 4KHSO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

If the concentrated acid and anhydrous salt are used, the reaction proceeds extremely slowly, but if a little water be added, it is complete at 180°.[2]

Potassium ferrocyanide, in addition to its use in the preparation of Prussian blue and other cyanogen compounds, is employed in calico-printing, and also for the case-hardening of iron. The commercial salt frequently contains considerable quantities of potassium sulphate, which can be removed by recrystallisation only with difficulty.

Sodium Ferrocyanide, $Na_4FeCy_6,10H_2O$, or *yellow Prussiate of Soda*, is manufactured as already described, and may be obtained also by boiling Prussian blue with caustic soda or sodium carbonate. It crystallises readily in large, monoclinic, pale yellow prisms, and effloresces slightly in the air; at 100° it loses the whole of the water, the residue being a white powder. One hundred parts of water dissolve about 27 parts of $Na_4FeCy_6,10H_2O$ at 15°, and about 160 parts at 100°.

Ammonium Ferrocyanide, $(NH_4)_4FeCy_6,3H_2O$, is obtained by the action of ammonia on ferrocyanic acid or on Prussian blue, and crystallises in yellow prisms isomorphous with the potassium salt. Its solution decomposes readily on heating, with evolution of ammonium cyanide. A dull green deposit of the formula $Fe^{III}Fe^{II}(NH_4)_8[Fe^{II}Cy_6]_4,3H_2O$ is produced on boiling the solution in contact with air.[3]

Ammonium ferrocyanide gives a double salt with ammonium chloride:[4] $(NH_4)_4FeCy_6,NH_4Cl,3H_2O$.

Calcium Ferrocyanide, $Ca_2FeCy_6,12H_2O$, is formed when Prussian blue is boiled with the requisite quantity of milk of lime, or by passing hydrogen cyanide into a mixture of slaked lime and ferrous hydroxide suspended in water. It forms pale yellow, triclinic prisms; one part dissolves in 0·66 part of water at 90°, and it is even more soluble in cold water. The salt is very efflorescent and the analytical results for the water of crystallisation are always somewhat lower than are required for $12H_2O$.[1] Measurements of the osmotic pressure and electrical conductivity of solutions of calcium and strontium ferrocyanides indicate that these salts are associated in solution.[2]

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[1] Everitt, *Phil. Mag.*, 1835, [3], **6**, 97.

[2] Adie and Browning, *Journ. Chem. Soc.*, 1900, **77**, 150.

[3] Williams, *Proc. Chem. Soc.*, 1913, **29**, 54.

[4] Briggs, *Journ. Chem. Soc.*, 1911, **99**, 1019.

Potassium Calcium Ferrocyanide, $K_2CaFeCy_6,3H_2O$, and *Ammonium Calcium Ferrocyanide*, $(NH_4)_2CaFeCy_6,3H_2O$, are obtained as white, crystalline precipitates, very sparingly soluble in water when calcium chloride is added to a moderately concentrated solution of potassium or ammonium ferrocyanide, or by the addition of potassium or ammonium chloride to a solution of calcium ferrocyanide.

Strontium Ferrocyanide, $Sr_2FeCy_6,14H_2O$, is most readily obtained by neutralising ferrocyanic acid with strontium hydroxide or carbonate. It is very soluble in water, and crystallises from concentrated solution in monoclinic prisms, which lose $7H_2O$ on standing in the air, and a further $6H_2O$ over sulphuric acid.

Barium Ferrocyanide, $Ba_2FeCy_6,6H_2O$, is obtained by boiling Prussian blue with baryta water, or by the action of ferrous sulphate on barium cyanide. It forms flat, monoclinic prisms soluble in 580 parts of cold and 116 parts of boiling water.

Barium Potassium Ferrocyanide, $K_2BaFeCy_6,3H_2O$.—This salt is deposited in small, yellow rhombohedra when boiling saturated solutions of 2 parts of potassium ferrocyanide and 1 part of barium chloride are mixed and allowed to cool. It dissolves in ·38 parts of cold and 9·5 parts of boiling water.

Magnesium Ferrocyanide, $Mg_2FeCy_6,12H_2O$, is prepared in a similar manner to the calcium salt, and crystallises in pale yellow needles which are exceedingly soluble in water. The crystals lose $5H_2O$ on standing in the air.

Zinc Ferrocyanide, Zn_2FeCy_6, is a white precipitate used in medicine.

Copper Ferrocyanide, $Cu_2FeCy_6 + aq.$, is a fine brown precipitate known as Hatchett's brown. If solutions of $CuSO_4$ and K_4FeCy_6 are allowed to come into contact without mixing, copper ferrocyanide is formed as a thin membrane at the common surface. This membrane is permeable to water, but impermeable to various dissolved substances, and on this ground has been extensively employed in the investigation of osmotic pressure.[1]

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[1] Colman, *Analyst*, 1910, **35**, 299. Compare Berkeley, Hartley, and Burton, *Phil. Trans.*, 1909, **209**, 180.

[2] Berkeley, Hartley, and Stephenson, *ibid.*, 319.

Treatment of copper ferrocyanide with boiling concentrated hydrochloric acid removes half the copper, giving the double hydrogen or acid salt, $CuH_2FeCy_6,4H_2O$, which is a yellow substance insoluble in water.[2] It readily decomposes alkali carbonates with evolution of carbon dioxide, and when boiled with alkali chlorides it liberates hydrochloric acid, forming double ferrocyanides such as $CuNaHFeCy_6$, $CuNaKFeCy_6$, and CuK_2FeCy_6.

The ferrocyanides of other heavy metals, for example, nickel, cobalt, and manganese, behave similarly.[2]

A large number of other ferrocyanides and double ferrocyanides have been prepared, many of which crystallise well.[3] Those of the heavy metals are mostly sparingly soluble or insoluble precipitates, some of which possess characteristic colours, as in the case of copper and uranium, and potassium ferrocyanide is therefore used as a reagent for these metals. The ferrocyanides of iron are described below.

FERRICYANOGEN COMPOUNDS.

574 *Ferricyanic Acid*, H_3FeCy_6.—This is obtained by decomposing the lead salt with dilute sulphuric acid, or, preferably, the silver salt with hydrochloric acid, and evaporating the solution at a moderate temperature. The acid crystallises in brown needles and has an astringent, acid taste.

Potassium Ferricyanide, or *Red Prussiate of Potash*, K_3FeCy_6, is formed when potassium ferrocyanide is treated with oxidising agents. It is obtained on the large scale by passing chlorine into a solution of the yellow prussiate:

$$2K_4FeCy_6 + Cl_2 = 2K_3FeCy_6 + 2KCl.$$

By repeated crystallisation it may be readily separated from the potassium chloride formed at the same time, and is obtained as large dark red, anhydrous monoclinic prisms, sp. gr. 1·8, which occur frequently in twin forms. Potassium ferricyanide possesses a faintly astringent and saline taste, and dissolves in water, giving a yellowish-brown solution, which on dilution becomes lemon-yellow. One hundred parts of water dissolve:[1]

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[1] Traube, *Archiv für Anatomie und Physiologie*, 1867, 124; Pfeffer, *Osmotische Untersuchungen* (Leipzig, 1877); Morse, *Amer. Chem. J.*, 1911, **45**, 558.

[2] Williams, *Proc. Chem. Soc.*, 1912, **28**, 317.

[3] Wyrouboff, *Ann. Chim. Phys.*, 1869, [4], **16**, 280; 1870, [4], **21**, 271; 1876, [5], **8**, 444; Messner, *Zeit. anorg. Chem.*, 1895, **8**, 368; Werner, *Zeit. anal. Chem.*, 1919, **58**, 23.

At	4·4°	10°	15·6°	37·8°	100°
K_3FeCy_6	33·0	36·6	39·7	58·8	77·6 parts,

and 82 parts at 104°, the boiling point of the saturated solution. It is only slightly soluble in alcohol. When exposed to light the solution becomes darker, and a blue precipitate is formed, potassium ferrocyanide remaining in solution. When the salt is heated in a flame it burns, and when mixed with ammonium nitrate and heated, the mixture detonates. It is a powerful oxidising agent, especially in alkaline solution, converting the monoxides of lead and manganese into dioxides, and forming potassium chromate and potassium ferrocyanide when boiled with a solution of chromium sesquioxide in potash:

$$6K_3FeCy_6 + Cr_2O_3 + 10KOH = 6K_4FeCy_6 + 2K_2CrO_4 + 5H_2O.$$

In solution it is reduced to ferrocyanide by sodium amalgam, and by hydrogen dioxide:

$$4K_3FeCy_6 + 2H_2O_2 = 3K_4FeCy_6 + H_4FeCy_6 + 2O_2.$$

It is also reduced by hydrogen sulphide, slowly in the cold, but rapidly on warming:[2]

$$6K_3FeCy_6 + 3H_2S = 4K_4FeCy_6 + K_2Fe(FeCy_6) + 6HCN + 3S.$$

Hydrochloric acid readily reduces it:[3]

$$K_3FeCy_6 + 3HCl = H_3FeCy_6 + 3KCl.$$
$$2H_3FeCy_6 + 2HCl \rightleftharpoons H_4FeCy_6 + Cl_2.$$

Chlorine is formed, and since this oxidises ferrocyanic acid to ferricyanic acid, the reaction is reversible, but it proceeds to completion if the chlorine is removed from the sphere of action by reduced silver. Because of their hydrolysis, the chlorides of iron, zinc, and aluminium behave in the same way as hydrochloric acid.

Potassium ferricyanide is quantitatively reduced by an alkaline solution of hydrazine sulphate. Nitrogen is evolved and measurement of its volume affords a method of estimating either of the reacting substances:[1]

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[1] Wallace, *Journ. Chem. Soc.*, 1855, 7, 80.

[2] Venditori, *Atti R. Accad. Lincei*, 1906, [5], 15, i, 370.

[3] Gillet, *Bull. Soc. chim. Belg.*, 1912, 26, 236.

$$4K_3FeCy_6 + 4KOH + N_2H_4 = 4K_4FeCy_6 + 4H_2O + N_2.$$

In a similar manner, hydroxylamine reduces it, nitrogen and nitrous oxide being evolved.[1]

Sodium Ferricyanide, $2Na_3FeCy_6,H_2O$, is obtained by the action of chlorine upon sodium ferrocyanide. It dissolves in 1·25 parts of boiling and 5·3 parts of cold water, and crystallises in ruby-red, four-sided, deliquescent prisms.

Ammonium Ferricyanide, $2(NH_4)_3FeCy_6,H_2O$, is obtained in a similar way to the other ferricyanides. It forms fine red, monoclinic prisms, easily soluble in water and permanent in he air.

Lead Ferricyanide, $Pb_3(FeCy_6)_2,16H_2O$, is formed by mixing ot solutions of the potassium salt and lead nitrate. It forms ark reddish-brown crystals slightly soluble in cold, and rather ore soluble in hot water.

The ferricyanides of most of the other heavy metals are recipitates, generally possessing a yellow, greenish-brown, or eddish-brown colour, whilst some of them, like that of tin and ercury, are colourless. A number of ferricyanides form stable ouble salts with mercuric cyanide.[2]

FERRO- AND FERRI-CYANIDES OF IRON.

575 As already mentioned (p. 1302), the double cyanides of ron were the earliest known cyanogen compounds, having been irst obtained in 1704. In spite, however, of much experimental vork by Berzelius, Liebig, Williamson, and others, the exact omposition and constitution of the various compounds formed y the interaction of ferro- and ferri-cyanides with ferrous and erric salts is still in many respects doubtful. This is largely wing to the fact that the preparation of these compounds in a tate of purity is very difficult, and, moreover, slight alterations n the conditions under which the interaction of iron salts and he ferrocyanides takes place have frequently a very great nfluence on the nature of the product.

576 *Ferrous Ferrocyanides.*—When ferrous sulphate is added o potassium ferrocyanide in cold neutral solution in absence of xygen, a white precipitate is obtained having the composition

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[1] Rây and Sen, *Zeit. anorg. Chem.*, 1912, 76, 380.

[2] Williams, *Proc. Chem. Soc.*, 1912, 28, 317.

$Fe^{II}K_2[Fe^{II}Cy_6]$. This oxidises with great rapidity in the air, yielding the β-soluble blue described below. In acid solution, a precipitate of similar composition is formed,[1] which, however, differs from the foregoing in being less readily oxidised, and yielding γ-soluble blue (p. 1317).

A third substance of the same composition, Everitt's salt, is obtained as an insoluble compound by the action of sulphuric acid on potassium ferrocyanide. It forms a pale yellow powder which is seen under the microscope to consist of doubly refractive crystals of a pale greenish colour. It is much less readily oxidised than either of the other compounds already described, but nitric acid or hydrogen dioxide converts it into Williamson's violet (p. 1317).

Ferrous Hydrogen Ferrocyanide, $H_2Fe^{II}[Fe^{II}Cy_6]$, corresponding to the last named salt, is obtained by heating ferrocyanic acid solution at 110–120°, and on oxidation yields a violet substance, $Fe^{III}H[Fe^{II}Cy_6]$, closely resembling Williamson's violet in appearance, but containing no alkali.

577 *Ferric Ferrocyanides.*—These substances are the most important of the iron–cyanogen derivatives, the various substances comprised under the general name of Prussian blue belonging to this class. They are obtained (1) by the interaction of ferric salts and ferrocyanides; (2) by the interaction of ferrous salts and ferricyanides; (3) by the oxidation of ferrous ferrocyanides; and (4) by the reduction of ferric ferricyanides. The compounds formed in the different ways, although they may have the same empirical composition, frequently differ in both physical and chemical properties.

The researches of Hofmann[2] have shown that all these compounds consist of ferrocyanic acid, in which the hydrogen is either wholly or partially replaced by ferric iron, or partly by ferric iron and partly by another metal, and all of them may be represented by one of the two simple formulæ: (1) $Fe_4^{III}[Fe^{II}Cy_6]_3$, and (2) $Fe^{III}X[Fe^{II}Cy_6]$, where X is either hydrogen or a monovalent metal. The molecular weight is, however, undoubtedly much higher than that shown by the simple formulæ, and the products having the same empirical composition but different chemical and physical properties are, in all probability, polymers of the simple molecule.

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[1] Compare Müller and Treadwell, *J. pr. Chem.*, 1909, [2], **80**, 170.

[2] *Annalen*, 1904, **337**, 1; 1905, **340**, 267; 1905, **342**, 364; 1907, **352**, 54; *J. pr. Chem.*, 1909, [2], **80**, 160. See also Vorländer, *Ber.*, 1913, **46**, 181.

With the single exception of one of the ferric ammonium ferrocyanides, none of these compounds has been obtained anhydrous or in the crystalline form. The remainder are all colloidal substances, which still retain water when dried for months over phosphorus pentoxide, and this water cannot be removed by heat without simultaneous decomposition of the compound. On account of their colloidal nature, it is extremely difficult to prepare them in a state of purity, as, like other similar substances, they obstinately retain salts, and on this account very varying formulæ have been attributed to them in the past by various workers.

All the ferric ferrocyanides possess an intensely blue or violet colour, and form valuable dyes, differing in this respect from all the other ferrocyanides, for although most of the latter are coloured, none of them can be described as colouring matters. Hofmann and Resenscheck[1] suggest that the cause of the intense colour is the presence in the same molecule of ferrous and ferric iron atoms; thus derivatives of the type $Fe^{II}K_2[Fe^{II}Cy_6]$ are colourless, whereas $Fe^{III}K[Fe^{II}Cy_6]$ is Prussian blue. They point out that similar intense colour is present in many other compounds containing an element in different stages of oxidation. For example, sulphur sesquioxide, S_2O_3, is of a deep indigo blue colour, whereas both sulphur dioxide and trioxide are colourless; red lead, in the same way, is more highly coloured than litharge or the dioxide; the tungsten bronzes furnish another example. It has also been supposed that the presence of chemically combined water was essential to the production of the colour, but the preparation of an anhydrous ferric ammonium ferrocyanide by Hofmann and Arnoldi[2] disproves this suggestion, as that substance is still intensely coloured.

a-Soluble Prussian Blue or *a-Ferric Potassium Ferrocyanide*, $4Fe^{III}K[Fe^{II}Cy_6],7H_2O$, is obtained by precipitating a solution of potassium ferrocyanide with slightly less than one equivalent of a ferric salt; the precipitate is washed by decantation with potassium chloride solution, and then with 70 per cent. alcohol, and dried over phosphorus pentoxide. It forms a voluminous mass, having a beautiful bronze reflex, and yields a deep blue powder. It dissolves in pure water, forming a deep blue solution, and like other colloids is precipitated by the addition of salts. It also dissolves readily in oxalic acid, and is quickly converted into ferrocyanide and ferric hydroxide by dilute ammonia. The water in the dried substance cannot be driven off without decomposition taking place, and is therefore probably "constitutional" water. Hofmann states that it is in all probability a basic ferric salt of the simplest formula $(HO)_2Fe^{III}[Fe^{II}Cy_6]KH_2$, two molecules of which have lost one molecule of H_2O, forming the anhydro-salt:

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[1] *Annalen*, 1905, **342**, 364.

[2] *Ber.*, 1906, **39**, 2204.

$$KH_2[Fe^{II}Cy_6]Fe^{III}(OH)\cdot O\cdot(HO)Fe^{III}[Fe^{II}Cy_6]KH_2.$$

When treated with dilute acid it loses potassium, yielding the corresponding *a-ferric hydrogen ferrocyanide*, $Fe^{III}H[Fe^{II}Cy_6]$ + aq., which closely resembles the ferric potassium salt, but is insoluble in water.

When a solution of potassium ferricyanide is precipitated with slightly less than one equivalent of ferrous salt, a soluble Prussian blue is produced, which its mode of formation would indicate to be a ferrous potassium ferricyanide, $Fe^{II}K[Fe^{III}Cy_6]$. It has, however, been shown by Skraup,[1] and by Hofmann, Heine, and Höchtlen,[2] that this substance is identical with that obtained in the manner already described from potassium ferrocyanide and a ferric salt. Evidence other than that of the method of formation is therefore necessary to decide whether the substance possesses the constitution (1) or (2).

(1)	(2)
Ferric Potassium Ferrocyanide.	*Ferrous Potassium Ferricyanide.*
$Fe^{III}K[Fe^{II}Cy_6]$.	$Fe^{II}K[Fe^{III}Cy_6]$.

Alkalis decompose it into potassium ferrocyanide and ferric hydroxide, which is in favour of the first formula, but this is not conclusive, inasmuch as potassium ferricyanide and ferrous hydroxide, which would be the products formed from a substance of the second formula, immediately interact, yielding ferrocyanide and ferric hydroxide. Hofmann has, however, shown that dilute hydrogen dioxide containing acid, which readily reduces the ferricyanogen group to ferrocyanogen, but has no effect on ferric salts, quickly reduces a ferric ferricyanide solution to Prussian blue, and also oxidises the ferrous ferrocyanides to Prussian blue. This must therefore contain the ferric iron as the basic constituent, and ferrous iron in the acidic radicle, as given in formula (1). In fact, all the blue iron–cyanogen compounds are *ferric* ferrocyanides, the *ferrous* ferricyanides apparently not being capable of permanent existence, intramolecular change taking place where their formation would be expected.

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[1] *Annalen*, 1877, **186**, 371.

[2] *Ibid.*, 1904, **337**, 1.

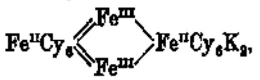
β-Soluble Prussian Blue, $Fe^{III}K[Fe^{II}Cy_6],H_2O$, is obtained by the oxidation of the ferrous potassium ferrocyanide obtained in neutral solution (p. 1313). It is soluble in water, and differs from the previous compound chiefly by its insolubility in oxalic acid.

γ-Soluble Prussian Blue is prepared in a similar manner by oxidising the ferrous potassium ferrocyanide obtained in cold acid solution. It is soluble in water, but is much more stable towards alkalis than the two previous compounds, and only loses the potassium with difficulty by the action of dilute acids or of ferric chloride.

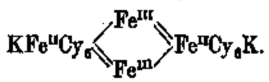
Williamson's Violet, $Fe^{III}K[Fe^{II}Cy_6],H_2O$.—This substance was first obtained by A. W. Williamson by the action of nitric acid or some other oxidising agent on Everitt's salt (p. 1314). It forms a deep violet-blue powder, which is transparent in thin layers, allowing green light to pass through. It is much more stable than any of the three compounds already described of the same empirical composition, being quite insoluble in mineral acids, which do not remove the potassium, and also in oxalic acid, and being only very slowly decomposed by dilute alkalis.

Hofmann regards γ-soluble blue and Williamson's violet as formed by the union of two molecules of the simple substance $Fe^{III}K[Fe^{II}Cy_6]$, the former having an unsymmetrical and the latter a symmetrical constitution, as shown by the formulæ:

γ-Soluble Blue.



Williamson's Violet.



In addition to the ferric potassium compounds, several ferric ammonium compounds have been prepared.

Monthiers' Blue, $Fe^{III}NH_4[Fe^{II}Cy_6],H_2O$, was first obtained by Monthiers[1] by the oxidation of the white precipitate formed by the action of ammoniacal ferrous chloride on potassium ferrocyanide, and given by him the formula $(Fe_2)_2(FeCy_6)_3,6NH_3,9H_2O$, but it has been shown by Hofmann, Arnoldi, and Hiendlmaier[2] to have the formula given above. It is also formed if any of the soluble Prussian blues be exposed to sunlight with ammonium oxalate solution, and the resulting white compound oxidised by hydrogen dioxide, but is most readily obtained by acting on a solution containing potassium ferrocyanide, ammonium chloride, and ammonia with iron wire, and oxidising the green precipitate with hydrogen dioxide. It is a deep blue powder having an enamel-blue reflex soluble in water and oxalic acid, and decomposed slowly by dilute alkalis.

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[1] *J. Pharm.*, 1846, [3], 9, 262.

[2] *Annalen*, 1907, 352, 54.

A crystalline anhydrous *ferric ammonium ferrocyanide*, $Fe^{III}NH_4[Fe^{II}Cy_6]$, is obtained together with nitroprusside by heating a solution of hydroxylamine hydrochloride with one of potassium ferrocyanide, and forms a deep blue, insoluble powder, which is seen under the microscope to consist of opaque violet-red, lustrous cubes. In its properties it very closely resembles Williamson's violet.[1]

Insoluble Prussian Blue, or *Ferric Ferrocyanide*, $Fe^{III}_4[Fe^{II}Cy_6]_3$ or Fe_7Cy_{18}, is prepared by precipitating a solution of a soluble ferrocyanide with an excess of ferric salt, or by the action of the latter on soluble Prussian blue. The exact composition of the precipitate depends on the proportions of ferric salt and ferrocyanide taken,[2] and it is exceedingly difficult to free it from the last traces of alkali. The precipitate is insoluble in water and dilute mineral acids, but dissolves in ammonium tartrate solution, forming a violet liquid, and in oxalic acid, forming a blue solution. The latter was formerly largely used as a blue ink, but has now been replaced by the blue aniline colours.

The dried substance contains water which cannot be driven off without decomposition, the amount corresponding approximately to the formula $Fe_7Cy_{18},9H_2O$, or $Fe_7Cy_{18},10H_2O$. When strongly heated in the air, it burns like tinder, forming ferric oxide, and it is decomposed by alkalis into ferric hydroxide and the ferrocyanide of the alkali employed. Concentrated sulphuric acid converts it into a white mass, neither iron nor hydrocyanic acid being removed, and when this is dried on a porous plate, an amorphous powder remains which is decomposed by water into Prussian blue and sulphuric acid (Berzelius). Prussian blue also dissolves in hot concentrated hydrochloric acid, forming a yellow solution from which ferrocyanic acid separates on standing. It dissolves more readily in a mixture of hydrochloric acid with ethyl alcohol or higher alcohols, or with amyl acetate, small quantities of water causing a blue precipitate in the solutions.[1]

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[1] Hofmann and Arnoldi, *Ber.*, 1906, **39**, 2204.

[2] Volschin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 480; Müller and Stanisch, *J. pr. Chem.*, 1909, [2], **79**, 81; **80**, 153.

Turnbull's Blue.—Gmelin obtained a blue compound by the precipitation of potassium ferricyanide with excess of ferrous salt, which was afterwards manufactured in England under the name of Turnbull's blue. From its mode of preparation it was supposed to be ferrous ferricyanide, $Fe_3^{II}[Fe^{III}Cy_6]_2$ or Fe_5Cy_{12}, but it has been found [2] that the compound thus formed, after it has been washed in presence of air, during which oxidation probably takes place, is identical with the insoluble Prussian blue obtained from ferric salts and ferrocyanides (see also p. 1314).

Another ferric ferrocyanide, differing from that above described, has been obtained by Hofmann and Resenscheck [3] by the action of hydrogen dioxide on a solution of ferric ferricyanide in presence of an excess of strong hydrochloric acid. It has the composition $Fe_7Cy_{18},10H_2O$. In colour and properties it resembles Williamson's violet, but is less stable towards dilute ammonium hydroxide. It is insoluble in oxalic acid.

Commercial Prussian Blue is a mixture of a number of the ferric ferrocyanides above described, and consequently varies considerably in its colour and appearance. It is sold in the form of lumps, powder, and paste. All these have a deep blue colour and show a bronze reflex in varying degree. The finest variety, known as Paris blue, is obtained by the precipitation of potassium ferrocyanide by a ferric salt, and the lumps of this product, especially when wet, have a splendid bronze lustre. As ferric salts are dear, the blue is usually made by precipitating a ferrocyanide with ferrous salt, and oxidising the product by an oxidising agent such as bleaching powder. The exact conditions are, however, mostly trade secrets.

Prussian blue is still employed as a dye, although to a less extent than formerly, having been to a considerable degree replaced by the coal-tar colours.

578 *Ferric Ferricyanides.*—When a ferric salt is added to a solution of a ferricyanide no precipitate is obtained, but the solution assumes a dark brown colour, and probably contains ferric ferricyanide, although no solid compound of that composition has been isolated from it.[4]

[1] Coffignier, *Bull. Soc. chim.*, 1902, [3], **27**, 696; Watson Smith, *J. Soc. Chem. Ind.*, 1903, **22**, 472.

[2] Hofmann, Heine, and Höchtlen, *Annalen*, 1904, **337**, 1. Compare, however, Müller and Stanisch, *J. pr. Chem.*, 1909, [2], **79**, 81; **80**, 153.

[3] *Annalen*, 1905, **340**, 267.

[4] See Haller, *Kolloid Zeit.*, 1917, **20**, 76.

Prussian Green.—When an excess of chlorine is allowed to act on a solution of a ferro- or ferri-cyanide, or on Williamson's violet, a green hydrated compound is precipitated, to which the name Prussian green has been given. The composition of this substance is variable, and numerous formulæ have been proposed for it, such as Fe_3Cy_8, Fe_5Cy_{14}, Fe_9Cy_{24}. It has, however, been shown by Messner[1] that when chlorine is passed through a boiling solution in the dark, until no further action takes place, and the precipitate is washed with water in the dark, the green product has the empirical formula $FeCy_3$, and is probably a polymeric ferric ferricyanide, $[Fe^{III}(Fe^{III}Cy_6)]_x$. It readily loses cyanogen, forming Prussian blue, this being the cause of the varying composition found by the former investigators. It is doubtful if the pure compound has a green colour, this being probably due to the presence of traces of Prussian blue.

IRON PENTACYANO-DERIVATIVES.

578 It has already been stated that one of the cyanogen groups in ferro- and ferri-cyanides can be replaced by other groups, forming stable salts, which in general properties are closely allied to these substances.

Carbonylferrocyanic Acid, $H_3[Fe^{II}(CO)Cy_5]$.—This acid is made by treating a suspension of the copper salt in water with hydrogen sulphide. It forms colourless crystals soluble in water. Its solution is acid to litmus and will decompose alkali carbonates.[2] The *potassium* salt is slowly formed by the action of carbonic oxide on boiling potassium ferrocyanide solution, the group CO replacing 1 molecule of potassium cyanide, which undergoes conversion into potassium formate and ammonia:[3]

$$K_4FeCy_6 + CO + 2H_2O = K_3Fe(CO)Cy_5 + NH_3 + H{\cdot}CO{\cdot}OK.$$

It forms pale yellow crystals containing $4H_2O$. The free acid forms colourless, crystalline plates.

The salts of this acid are almost invariably present in the crude ferrocyanides obtained from coal-gas, their formation being due to the carbonic oxide always present in the gas. They are readily separated by treatment with dilute alcohol, in which the carbonylferrocyanides are soluble, and the ferrocyanides insoluble.[4]

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[1] *Zeit. anorg. Chem.*, 1895, **9**, 136.

[2] Muller, *Ann. Chim. Phys.*, 1889, [6], **17**, 93.

[3] *Ibid.*, *Compt. rend.*, 1898, **126**, 1421.

[4] Compare Lecocq, *Bull. Soc. chim. Belg.*, 1911, **25**, 72.

With ferric chloride the carbonylferrocyanides give a precipitate of *ferric carbonylferrocyanide*, $Fe^{III}[Fe^{II}(CO)Cy_5] + aq.$, which differs from Prussian blue in possessing an intense purple colour. The *copper* salt is pale apple-green.

Nitroprussic Acid or *Nitrosoferricyanic Acid*, $H_2[Fe^{III}(NO)Cy_5]$.—Gmelin and other chemists observed that the coffee-brown solution obtained by the action of nitric acid on potassium ferrocyanide yields a splendid purple-red colour when treated with the sulphides of the alkalis. Playfair,[1] in 1849, showed that this reaction is produced by the presence of a peculiar compound which is formed by the action of nitric acid on ferro- or ferri-cyanides, which he termed nitroprussic acid, and which may be regarded as ferricyanic acid in which one of the Cy groups has been replaced by the nitroso-group NO.

The acid is formed when nitric oxide is passed into an acid solution of potassium ferrocyanide, the ferrocyanic acid, after oxidation to ferricyanic acid, acting with nitric oxide thus:

$$H_3FeCy_6 + NO = H_2[Fe(NO)Cy_5] + HCy.$$

The potassium salt is formed also by the action of potassium nitrite on a mixture of potassium cyanide and a ferrous salt:

$$5KCy + 2FeSO_4 + KNO_2 + H_2O = K_2[Fe(NO)Cy_5] + Fe(OH)_2 + 2K_2SO_4,$$

the ferrous hydroxide being further converted into ferric hydroxide,[2] with liberation of ammonia, by the action of the nitroprusside or the nitrite.

Nitroprussides may be prepared from either ferrocyanides or cyanides. In the former case powdered potassium ferrocyanide is treated with double its weight of strong nitric acid previously mixed with an equal volume of water. The coffee-coloured solution evolves carbon dioxide, nitrogen, cyanogen, and hydrocyanic acid, and as soon as solution is complete it is warmed on the water-bath till a portion of the liquid gives only a slate-coloured precipitate with ferrous sulphate. On cooling, the liquor is poured off from the separated potassium nitrate, and neutralised with sodium carbonate. The solution is then concentrated, filtered, and the nitrates separated by fractional crystallisation, or the copper salt may be precipitated and decomposed, after washing, with soluble bases.

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[1] *Phil. Trans.*, 1849, **139**, 477.

[2] Städeler, *Annalen*, 1869, **151**, 1. See also Schwarzkopf, *Abhandl. deut. naturwiss.-med. Ver. Böhmen*, 1911, **3**.

To obtain them from cyanides, a concentrated aqueous solution of ferrous sulphate is mixed with a solution of equal parts of potassium cyanide and sodium nitrite, and allowed to remain for five hours at the ordinary temperature. Ferric hydroxide separates, and nitrogen and nitric oxide are evolved. The solution is then heated to 25°, made slightly alkaline with caustic soda, filtered, and the salt crystallised out.

Nitroprussic acid is formed by decomposing the silver salt with hydrochloric acid, or the barium salt with dilute sulphuric acid. The red, strongly acid solution leaves on evaporation in a vacuum dark red, deliquescent, prismatic needles. This compound is very unstable and partially decomposes during the concentration of the liquid with formation of ferric hydroxide, hydrocyanic acid, etc.

Potassium Nitroprusside, $K_2[Fe(NO)Cy_5]$, forms dark red soluble, deliquescent, monoclinic prisms.

Sodium Nitroprusside, $Na_2[Fe(NO)Cy_5],2H_2O$, crystallises most readily of all the nitroprussides, and is usually prepared by concentrating the solution obtained as above described until a sufficient quantity of nitroprusside has crystallised out. This is then removed from the warm solution in order to avoid any admixture of nitrates. It is purified by crystallisation and forms large ruby-red, rhombic prisms. It dissolves in 2·5 parts of water at 15°, and is more soluble in hot water. When exposed to light, the solution decomposes with separation of Prussian blue and nitric oxide, but may be kept unaltered in the dark for a long time, especially if a trace of sulphuric acid be present.[1]

Hydrochloric acid attacks sodium nitroprusside, giving hydrogen cyanide and ferric chloride, which reacts with the excess of nitroprusside to form ferric nitroprusside.[2] Concentrated sulphuric acid also attacks it, carbon monoxide being evolved. The reactions are very complex.[3] Boiled with caustic soda, it yields ferrous hydroxide, sodium ferrocyanide, and sodium nitrite.

Sodium nitroprusside is readily reduced by sodium amalgam or the zinc–copper couple to sodium ferrocyanide. In neutral solution the nitrogen is evolved as such, in alkaline solution as ammonia, and in acid solution part of it as hydrogen cyanide, Prussian blue also being formed[4]

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[1] Zuccari, *Ann. Chim. Applicata*, 1914, **2**, 287; 1915, **3**, 277.

[2] Bhaduri, *Zeit. anorg. Chem.*, 1913, **84**, 95.

[3] Bhaduri, *loc. cit.*; Pereira, *Anal. Fís. Quím.*, 1915, **13**, 166.

[4] Bhaduri, *loc. cit.*

The nitroprussides of ammonium and of the alkaline-earth metals also form red, easily soluble salts, their solutions decomposing on standing or on boiling, with separation of Prussian blue and ferric oxide. The silver salt and the ferrous salt are flesh-coloured precipitates.

The splendid purple colour which the nitroprussides impart to a solution of an alkaline sulphide is very characteristic, and this reaction is employed both for the detection of alkali sulphides and of small quantities of alkalis and alkaline earths in solution, by passing a little sulphuretted hydrogen through the liquid in the latter case and then adding a few drops of nitroprusside solution. The purple compound thus produced is very unstable; its constitution is uncertain, but is very probably represented by the formula $Na_3[Fe^{II}(O{:}N{\cdot}SNa)Cy_5]$, as Hofmann,[1] by the action of thiourea, $CS(NH_2)_2$, on sodium nitroprusside, has obtained the compound $Na_3[Fe^{II}(O{:}N{\cdot}SCNH{\cdot}NH_2)Cy_5]$, which forms a beautiful carmine-red powder, closely resembling in its properties the substance formed from nitroprussides and sulphides.

Starting from sodium nitroprusside, Hofmann has obtained the following substituted ferro- and ferri-cyanides:

Sodium nitroferrocyanide,	$Na_4[Fe^{II}(NO_2)Cy_5],10H_2O$,
Potassium nitroferricyanide,	$K_3[Fe^{III}(NO_2)Cy_5]$,
Sodium aquoferrocyanide,	$Na_3[Fe^{II}(H_2O)Cy_5],7H_2O$,
Sodium aquoferricyanide,	$Na_2[Fe^{III}(H_2O)Cy_5]$,
Sodium ammonioferrocyanide,	$Na_3[Fe^{II}(NH_3)Cy_5],6H_2O$,
Sodium ammonioferricyanide,	$Na_2[Fe^{III}(NH_3)Cy_5],H_2O$,
Sodium sulphitoferrocyanide,	$Na_5[Fe^{II}(SO_3)Cy_5],9H_2O$,
Sodium arsenitoferrocyanide,	$Na_4[Fe^{II}(AsO_2)Cy_5],10H_2O$.

The substituted ferrocyanides are yellow or reddish-yellow, crystalline salts, which give blue precipitates with ferric salts, and brownish-red precipitates with copper salts. The substituted ferricyanides have a deep carmine-red or purple colour, and give no precipitate with ferric salts, and pale green precipitates with copper salts. All these compounds are converted into sodium ferrocyanide by boiling with sodium cyanide solution.

IRON THIOCYANATES.

580 *Ferrous Thiocyanate*, $Fe(SCN)_2,3H_2O$, is obtained in large pale-green, monoclinic crystals by dissolving iron wire

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[1] *Annalen*, 1900, **312**, 1. Compare Virgili, *Zeit. anal. Chem.*, 1906, **45**, 409.

in concentrated thiocyanic acid and evaporating the liquid in absence of air. The salt dissolves readily in water, alcohol, or ether, and becomes red-coloured on exposure to the air.

Ferric Thiocyanate, $\mathrm{Fe(SCN)_3,3H_2O}$.—This compound is obtained in the pure state when a mixture of anhydrous ferric sulphate and potassium thiocyanate in equivalent proportions is treated with alcohol and the solution evaporated over sulphuric acid in a vacuum. Dark red or almost black cubical crystals are deposited, and these dissolve readily in water, alcohol, or ether. The production of this intense colour on the addition of a thiocyanate serves as a delicate test for ferric salts in solution. If a concentrated aqueous solution is shaken with ether it becomes colourless and the ether attains a purple-red colour. The aqueous solution is also decolorised in presence of reducing agents as well as on treatment with mercuric chloride or gold chloride.

A solution of ferric thiocyanate is not permanent, and the colour gradually fades when the solution is allowed to stand at the ordinary temperature.[1] This bleaching is due to the progressive reduction of the iron to the ferrous condition, and in the corresponding oxidation of thiocyanate which occurs, carbon dioxide, sulphuric acid, and ammonia are formed.[2]

The reaction between a ferric salt and potassium thiocyanate in aqueous solution is not complete when equivalent quantities are employed, and the state of equilibrium produced in any mixture of the two depends on the dilution, the temperature, and the relative proportion of the two salts present.[3] When the deep red solution is diluted so as to be almost colourless addition of potassium thiocyanate restores the colour.

The iron thiocyanates form double salts with other thiocyanates, which are analogous to the ferro- and ferri-cyanides, and have the general formulæ $\mathrm{M^I_4Fe(CNS)_6}$ and $\mathrm{M^I_3Fe(CNS)_6}$. Unlike these, however, they are very unstable substances and are completely dissociated by water into the constituent salts.[4]

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[1] See, for example, Oerum, *Zeit. anal. Chem.*, 1904, **43**, 152; Stokes and Cain, *J. Amer. Chem. Soc.*, 1907, **29**, 412, 445.

[2] Philip and Bramley, *Journ. Chem. Soc.*, 1913, **103**, 795.

[3] Krüss and Moraht, *Ber.*, 1889, **22**, 2061; *Zeit. anorg. Chem.*, 1892, **1**, 399; Magnanini, *Zeit. physikal. Chem.*, 1891, **8**, 1; Vernon, *Chem. News*, 1892, **66**, 177 *et seq.*; 1893, **67**, 66; Gladstone, *ibid.*, 1893, **67**, 1.

[4] Rosenheim and Cohn, *Zeit. anorg. Chem.*, 1901, **27**, 280.

IRON AND SILICON.

581 *Silicides of Iron.*—Iron can readily be alloyed with silicon, and since silica and silicates are reduced by carbon in the presence of iron, all cast iron contains silicon, probably as a silicide.

The compound Fe_2Si is obtained by heating iron or ferric oxide with silicon in the electric furnace, and forms magnetic prisms of specific gravity 7. It is readily attacked by hydrofluoric acid,[1] and by sulphur chloride.[2]

Compounds of the formulæ FeSi, $FeSi_2$, and Fe_3Si_2 have also been described.[3]

Mixtures of iron and silicon, known as "ferro-silicon" and containing up to 90 per cent. silicon, are prepared in the electric furnace on a large scale. Under certain conditions ferro-silicon is liable to decompose, giving off poisonous gases.[4]

Silicates of Iron.—Several ferrous and ferric silicates occur in the mineral kingdom, but they are more frequently found as double silicates, in which the alkali metals and the metals of the alkaline earths are present. These are generally isomorphous mixtures in which ferric oxide is replaced by alumina, whilst lime, magnesia, and the alkalis are substituted by ferrous oxide, manganous oxide, etc. For a description of these compounds works on mineralogy must be consulted.

The Iron Tree.—In Glauber's description of the preparation of *oleum martis* (p. 1277) the following passage occurs:—"When such a red *massa* before it deliquesces to an *oleum* is laid in *oleum arenæ vel silicum* (the modern sodium silicate) for one or two hours, a tree grows out of it, with roots, stems, many branches, and twigs, wonderful to behold." This phenomenon depends upon the fact that water-glass, which contains always some carbonate, decomposes the ferric chloride into ferric silicate and basic ferric carbonate, whilst bubbles of carbon dioxide are given off, and thus filiform processes are produced. In place of the ferric chloride, ferrous chloride, cobalt chloride, nickel chloride, copper nitrate, and many other easily soluble metallic salts may be employed, and thus a series of differently coloured coral-like growths may be produced.

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[1] Moissan, *Compt. rend.*, 1895, **121**, 621.

[2] Nicolardot, *Ibid.*, 1908, **147**, 676.

[3] Compare Guertler and Tammann, *Zeit. anorg. Chem.*, 1905, **47**, 163; Vigouroux, *Compt. rend.*, 1905, **141**, 828; Vanzetti, *Gazz.*, 1906, **36**, i, 498. Murakami, *Sci. Rep. Tohoku. Imp. Univ.*, 1921, **10**, 79.

[4] See *Zeit. Nahr. Genussm.*, 1906, **12**, 132; *J. Soc. Chem. Ind.*, 1907, **26**, 968; 1909, **28**, 25, 143; 1910, **29**, 154, 280, 355, 955; *Stahl und Eisen*, 1912, **32**, 267.

DETECTION AND ESTIMATION OF IRON.

582 A bead of microcosmic salt or borax is coloured dark-green by ferrous salts. This colour readily changes to a yellow or reddish-brown by oxidation. On cooling, the colour becomes less distinct, disappearing altogether if only traces of ferric oxide are present. Iron can also be detected in the dry way by Bunsen's test. For this purpose, the compound is heated on the end of a carbonised wooden match, which has previously been impregnated with fused sodium carbonate, held in the reduction zone of the non-luminous gas flame. The whole is then rubbed up in an agate mortar with a little water, the particles of iron being extracted on the point of a magnetised knife-blade. The adhering particles of finely divided iron are brought on to a small piece of filter paper, dissolved in a drop of aqua regia, and a drop of potassium ferrocyanide added, this confirmatory test being necessary since nickel and cobalt are also magnetic.

The iron compounds do not impart any colour to the non-luminous gas flame. The spectrum of the metal is extraordinarily rich in lines, more than 4,500 having been measured. A dark line in the solar spectrum corresponds to each of the bright lines in the visible part of the spectrum.

In solution, ferrous salts immediately give a dark blue precipitate with potassium ferricyanide, whilst ferric salts are coloured dark brown by this reagent, no precipitate being formed. Ferric salts give a blue coloration or precipitate with potassium ferrocyanide, and ferrous salts, which, owing to absorption of oxygen usually contain larger or smaller quantities of ferric salts, give a bluish-white precipitate, and this on shaking with air assumes a dark blue colour. Ferric salts are readily detected by the blood-red coloration which they produce with soluble thiocyanates.

With alkalis ferrous salts give a white, or usually greenish precipitate, which quickly changes to a dark-green colour on exposure to air, and afterwards becomes brown. Ferric salts at once give a reddish-brown precipitate.

It has been stated already that manganese is obtained together with iron in the course of qualitative analysis and the mode of their separation has been described. The precipitate containing ferric hydroxide may also contain uranium. This is readily separated by digesting the precipitate with a concentrated solution of ammonium carbonate. The washed residue is then dissolved in hydrochloric acid and the confirmatory test for iron applied.

In the processes of *quantitative analysis* iron is estimated both gravimetrically and volumetrically. In the first case the iron must be present as ferric salt. Ferrous salts are, therefore, previously oxidised with nitric acid and then precipitated with ammonia, the precipitate is washed with boiling water, dried, ignited, and weighed as the sesquioxide. If the solution should contain tartaric acid, sugar, or other organic compounds, ammonia produces no precipitate. In these cases the iron must be previously precipitated as sulphide; this is well washed with water containing ammonium sulphide, dissolved in nitric acid and the iron precipitated with ammonia; or the organic compound may be destroyed by ignition. If other metals precipitable by ammonia and ammonium sulphide are present, the iron can be separated by adding sodium or ammonium formate, acetate, or succinate to the neutral solution and boiling, when basic ferric formate, acetate, or succinate is thrown down. This is filtered whilst hot, washed with boiling water, dried, ignited, and weighed as ferric oxide. The precipitate may contain alumina, and this must then be separated by means of caustic potash. For the separation of iron from various other metals the use of nitrosophenylhydroxylamine, known as "cupferron," has been proposed.[1]

The chief *volumetric* processes for the estimation of iron depend upon the amount of oxygen required to convert it from the ferrous into the ferric form, and the solutions to be tested must first have the iron completely reduced to the ferrous state. For this purpose many reducing agents may be employed, the methods most frequently used being (1) treatment with zinc or aluminium in acid solution, (2) treatment with sulphuretted hydrogen, (3) boiling with ammonium bisulphite solution, (4) addition of stannous chloride to the boiling solution, and (5) shaking the solution acidified by hydrochloric acid with a little mercury.[2] In the case of (2) and (3) the excess of reducing agent is removed by boiling, and in (4) the excess of stannous chloride is precipitated by addition of mercuric chloride.

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[1] Baudisch, *Chem. Zeit.*, 1909, **33**, 1298; Biltz and Hödtke, *Zeit. anorg. Chem.*, 1910, **66**, 426; Fresenius, *Zeit. anal. Chem.*, 1911, **50**, 35.

[2] McCay and Anderson, *J. Amer. Chem. Soc.*, 1921, **43**, 2372.

The oxidising medium employed is a standard solution of potassium permanganate or dichromate, these being standardised by means of pure iron wire, recrystallised oxalic acid, or pure ferrous ammonium sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$, the latter containing exactly one-seventh of its weight of iron. In carrying out the permanganate method, the ferrous solution prepared as above described is acidified with sulphuric acid and titrated with the permanganate solution until a permanent pink coloration is produced. Permanganate cannot, however, be used when hydrochloric acid is present without special precautions, and in that case it is better to employ dichromate, which may also be used in presence of sulphuric acid. The completion of the reaction is ascertained in this case by bringing a drop of the solution in contact with a very dilute freshly prepared solution of potassium ferricyanide, free from ferrocyanide, on a white porcelain plate; the dichromate is added until no blue coloration is obtained.

Methods have also been proposed for the direct volumetric estimation of ferric iron, without a preliminary reduction to the ferrous state. The reducing agent chiefly employed for this purpose, in the form of a standard solution, is titanium trichloride (p. 842), potassium thiocyanate being added as indicator to the acidified solution of the ferric salt. The titration is carried out in an atmosphere free from oxygen, and the addition of titanium trichloride is continued until the red colour due to ferric thiocyanate has disappeared.[1]

The Atomic Weight of iron has been accurately determined by several chemists. Svanberg and Norlin,[2] by reducing the oxide in hydrogen, obtained the number 56·09; Berzelius found 56·05 by oxidising the metal with nitric acid, and Erdmann and Marchand,[3] who reduced the oxide in hydrogen, obtained 56·02. Maumené,[4] dissolving pure iron wire in nitric acid and precipitating with ammonia, found the number 56·00; and Dumas,[5] by the analysis of ferric chloride, obtained 56·23, whilst the analysis of ferrous chloride gave 56·09. By the reduction of ferric oxide, obtained from carefully purified ferric nitrate, with hydrogen, Richards and Baxter obtained the value 55·88 and from the amount of silver bromide yielded by ferrous bromide, the number 55·85.[1] The value at present (1922) adopted is 55·84.

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[1] See Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis* (Longmans, 1910).

[2] *Annalen*, 1844, **50**, 432.

[3] *Ibid.*, **58**, 212.

[4] *Ann. Chim. Phys.*, 1850, [3], **30**, 380.

[5] *Ibid.*, 1859, [3], **55**. 157.

An examination of the mass spectrum of iron indicates that the element is a simple one and not a mixture of isotopes. The atomic weight as given by this method is 55·91 ± 0·05. There is possibly an isotope present in very small amounts of atomic weight 54.[2]

COBALT. Co = 58·97. At. No. 27.

583 The word cobalt occurs in the writings of Paracelsus and Agricola as well as in those of "Basil Valentine"; two meanings were attached to this name; in the first place it signified a sprite or goblin supposed to haunt the mine, whilst in the second place it was used to denote certain minerals, which are too imperfectly described for exact identification. It appears, however, that in this latter sense it was employed to designate minerals which, although they possessed the appearance of a well-known metallic ore, did not yield any of this metal when subjected to the usual treatment. Hence the word came to signify a false ore. In later times the same name was given to the mineral which was used for the purpose of colouring glass blue, and is still employed for the preparation of smalt. In 1735, Brandt stated that the blue colour of smalt depends upon the presence of a peculiar metal to which he gave the name kobalt-rex, and in 1742 he showed that the colour of smalt does not depend, as had been believed, upon the presence of arsenic and iron, metals which are usually found in cobalt ores, for he found that some of these ores occur free from arsenic, and that these likewise give the blue colour. The new metal was stated to be magnetic and extremely infusible. These observations were confirmed by Bergman in 1780.

Cobalt does not occur in the free state in nature, and its ores, which usually contain nickel, are not very widely distributed. It is found as linnaeite, $(Co,Ni,Fe)_3S_4$; skutterudite, $CoAs_3$; speiss-cobalt or smaltite, $(Co,Ni,Fe)As_2$; cobaltite or cobalt glance, $(Co,Fe)AsS$; earthy cobalt, or wad, $(CO,Mn)O,2MnO_2,4H_2O$; erythrite, or cobalt bloom, $Co_3(AsO_4)_2,8H_2O$, etc.

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[1] *Zeit. anorg. Chem.*, 1900, 23, 245; 1904, 38, 232. Compare Baxter and others, *J. Amer. Chem. Soc.*, 1911, 33, 319, 337; 1912, 34, 1657.

[2] Aston, *Nature*, 1922, 110, 312.

The bulk of the cobalt of commerce is obtained from the district surrounding Cobalt city, in Ontario, where there are rich silver ores containing a notable proportion of cobalt and nickel, chiefly as arsenides. Deposits of oxides and sulphides of cobalt and nickel occur also in New Caledonia. Cobalt is almost always found as a constituent of meteoric iron, and its presence has been detected in the solar atmosphere.

Treatment of Cobalt Ores.—For the preparation of cobalt compounds, speiss-cobalt or other arsenical ores are employed. These, after roasting or calcination in the air, yield an impure cobalt arsenate which comes into commerce under the name of *zaffre*, and is further worked up as hereafter described. The cobalt ores, however, mostly contain large quantities of nickel and iron as well as other metals, and for this reason they are usually smelted in order to get rid of the greater part of the iron, the process employed being similar to that which is used for the extraction of copper. The roasted ore is fused with a flux of calcium carbonate or sand, when the iron slag flows on to the surface while the cobalt remains below as a heavy *speiss* or stone. The roasted ore or the speiss is then dissolved in strong hydrochloric acid, any arsenate of iron which may be present being precipitated by the careful addition of bleaching powder solution and a small quantity of milk of lime; the clear supernatant liquid is drawn off, treated with sulphuretted hydrogen for the purpose of separating copper, bismuth, etc., and the oxide of cobalt is then precipitated from the clarified solution by bleaching powder. The oxide thus obtained is washed and ignited, and this is brought into the market and largely used for colouring glass and porcelain, as well as for the preparation of the chloride and nitrate of cobalt. This oxide usually contains iron, nickel, and other impurities.

In the case of the New Caledonia ores, consisting chiefly of sulphides, the cobalt, nickel, etc., are converted into sulphates either by careful calcination at a moderate temperature, or by treatment with ferrous sulphate solution. The cobalt is then separated from the other metals which form soluble sulphates, and is finally obtained as oxide.

A small amount of cobalt is extracted in the form of oxide by the treatment of ores and metallurgical products containing nickel by a wet method. These materials are roasted sweet (*i.e.*, free from sulphur and arsenic), and the oxides thus formed dissolved in hydrochloric or sulphuric acid. The solution is then treated as described above for the separation of iron, the metals which are precipitated by sulphuretted hydrogen, and cobalt. The liquid resulting from the separation of the cobalt is further treated with milk of lime for the separation of nickel hydroxide, which is afterwards reduced to metal.[1]

584 *Preparation of Metallic Cobalt.*—This metal is obtained as a grey powder by igniting the oxide in a current of dry hydrogen or carbon monoxide, or by reduction of the oxide with carbon or aluminium.[2] By strongly heating the oxalate under a layer of powdered glass the metal can be obtained as a coherent mass, and this may be fused to a regulus by heating it in a crucible made of lime, magnesia, or graphite.

Pure cobalt may be obtained, according to Winkler,[3] by electrolysing a solution of pure cobalt sulphate in presence of ammonium sulphate and ammonia, platinum electrodes being used. The metal thus deposited invariably contains a small amount of oxygen (0·2—0·3 per cent.), and must therefore be heated in pure hydrogen. Pure metallic cobalt may be obtained also by heating cobalt carbonyl to a suitable temperature.[4]

Cobalt possesses the colour of polished iron; it is, however, harder than this metal. It melts at 1490°,[5] and may be distilled in the electric furnace.[6] It is malleable and very tough; it is magnetic up to 1150°, and has a specific gravity of 8·8 at 15°.[7] Cobalt in the form of powder absorbs oxygen from the air, often with ignition; the compact metal, however, does not undergo change at the ordinary temperature, but slowly oxidises when heated, and at a very high temperature burns with a red flame. The metal burns also at 150° in nitric oxide, forming the monoxide.[8] It is capable of absorbing 59–153 volumes of hydrogen, according to the physical state of the metal and the temperature. The metal is readily soluble in hydrochloric, dilute sulphuric, and nitric acids, and decomposes steam at a red heat. It may exist in the passive state, but exhibits this property to a less extent than nickel.[1]

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[1] For other methods of treating cobalt ores, see Pedersen, *Metallurgie*, 1911, **8**, 335; Barth, *ibid.*, 1912, **9**, 199.

[2] See *Report on Reduction of Cobalt Oxide; Department of Mines, Canada*, 1913, No. 259.

[3] *Zeit. anorg. Chem.*, 1895, **8**, 1.

[4] Eng. Patent 13207; 20/6/1908.

[5] Day and Sosman, *Amer. J. Sci.*, 1910, **29**, 161. See also Kalmus and Harper, *J. Ind. Eng. Chem.*, 1915, **7**, 6.

[6] Moissan, *Annalen*, 1906, **351**, 510.

[7] Copaux, *Compt. rend.*, 1905, **140**, 657. See also Kalmus and Harper, *loc. cit.*

[8] Sabatier and Senderens, *Compt. rend.*, 1892, **114**, 1429.

Cobalt combines with boron to form a crystalline compound which resembles the corresponding nickel compound, and is obtained in a similar manner.[2]

The character of the alloys which cobalt forms with other metals has been investigated by the method of thermal analysis, controlled by microscopic observations.[3]

Nickel and cobalt separate from their fused mixtures in mixed crystals, the composition of which is approximately that of the liquid from which they are deposited.[4]

Cobalt may be used for electroplating. A solution of 200 grams per litre of crystalline cobalt ammonium sulphate gives satisfactory coatings with a current density of 4 amperes per sq. dcm., but current densities up to 26 amperes per sq. dcm. may be employed with a solution made as follows: cobalt sulphate, 312 grams; sodium chloride, 19·6 grams; boric acid, nearly to saturation; water, 1 litre. The deposition is then very much more rapid and the deposit much harder than in the case of nickel, so that thinner coatings suffice and they are also superior in appearance.[5]

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[1] Hittorf, *Zeit. physikal. Chem.*, 1900, **34**, 385; Byers, *J. Amer. Chem. Soc.*, 1908, **30**, 1718; Byers and King, *J. Amer. Chem. Soc.*, 1919, **41**, 1902.

[2] See du Jassonneix, *Compt. rend.*, 1907, **145**, 240.

[3] See Sahmen, *Zeit. anorg. Chem.*, 1908, **57**, 1; Gwyer, *ibid.*, 113; Lewkonja, *ibid.*, **59**, 293; Ducelliez, *Bull. Soc. chim.*, 1911, [4], **9**, 1017; Hiege, *Zeit. anorg. Chem.*, 1913, **83**, 252; Raydt and Tammann, *ibid.*, 246; Kreiz, *Metall und Erz*, 1922, **19**, 137.

[4] Guertler and Tammann, *Zeit. anorg. Chem.*, 1904, **42**, 353; Ruer and Kaneko, *Metallurgie*, 1912, **9**, 422. See also Ruer and Kaneko, *Ferrum*, 1913, **10**, 257.

[5] Kalmus, Harper, and Savell, *J. Ind. Eng. Chem.*, 1915, **7**, 379.

COMPOUNDS OF COBALT.

Cobalt and Oxygen.

585 Cobalt forms three well-defined oxides:

Cobalt monoxide, CoO,
Cobalt sesquioxide, Co_2O_3,
Tricobalt tetroxide, Co_3O_4.

In addition to these, the dioxide, CoO_2, probably exists, and several others such as Co_8O_9,[1] Co_6O_7,[2] Co_4O_5,[3] and Co_3O_5[4] have been described,[5] but are probably mixtures.[6]

Of these oxides, the first, CoO, is a well-marked basic oxide, corresponding to the stable cobaltous salts in which the metal is divalent. The sesquioxide acts as a feebly basic oxide; the corresponding salts are unstable and are easily reduced to cobaltous salts. The dioxide appears to have a decided acidic function, and several stable cobaltites are known.

Cobalt Monoxide or Cobaltous Oxide, CoO.—This compound is the stable oxide of cobalt when calcination takes place at 1000° and may be obtained by reducing the higher oxide by heating it either in a current of hydrogen to a temperature not above 250°, or in a current of carbon dioxide to redness until its weight is constant (Russell).[7] It is a light brown powder, which does not alter in the air at the ordinary temperature. When heated in the electric furnace, it melts and yields rose-coloured needles.

Cobaltous oxide combines with certain metallic oxides when they are heated together, a flux such as potassium chloride being usually employed. With others, it forms solid solutions. Many of these substances are beautifully coloured and are used as paints and pigments. With aluminium oxide at 1100°, a blue compound, CoO,Al_2O_3, is produced, and above this temperature a green one of the composition $4CoO,3Al_2O_3$.[8] The blue substance is known as *Cobalt blue*, *Cobalt ultramarine*, *Thenard's blue*, or *Azure blue*. Its exact colour and composition depend upon the method of preparation, and as the cobalt is sometimes precipitated with sodium phosphate or arsenate it may contain cobalt phosphate and arsenate. With stannic oxide, the dark green compound, $2CoO,SnO_2$, that is, cobalt orthostannate, Co_2SnO_4, is obtained.[1] If excess of stannic oxide be employed, the resulting mass acquires a blue shade, and the greater the excess the more pronounced does the blue colour become. This substance is also manufactured and known as *Cœruleum*, *Cœline*, or *Bleu Celeste.* With zinc oxide, the green cobalt zincate is produced, and this forms solid solutions with excess of zinc oxide.[2] The substance is known as *Cobalt green*, or *Rinmann's green.* With chromic oxide a green chromite, CoO,Cr_2O_3, is obtained [2] which in the presence of excess of the oxide gives a bluish mass the exact shade of which depends upon the proportions of the oxides. It is known as *New blue.* A green vanadate, a tantalate, CoO,Ta_2O_5, and a yellow uranate have also been observed.[2] With magnesium oxide, cobalt oxide forms solid solutions the colour of which depends on the relative proportions of the oxides and varies from light to dark red.[3] The mass is known as *Cobalt red.* Solid solutions also result with manganous oxide and with nickelous oxide.[4]

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[1] *Zeit. anal. Chem.*, 1868, **7**, 336; *J. pr. Chem.*, 1856, **69**, 131.

[2] *Pogg. Ann.*, 1844, **61**, 472; 1851, **84**, 560.

[3] *Jahresber.*, 1868, 265.

[4] *Journ. Chem. Soc.*, 1890, **58**, 1213.

[5] See also Taylor, *Mem. Manch. Phil. Soc.*, 1903, [5], **12**, 1.

[6] See Wöhler and Balz, *Zeit. Elektrochem.*, 1921, **27**, 406.

[7] *Journ. Chem. Soc.*, 1863, **16**, 51.

[8] Hedvall, *Arkiv Kem. Min. Geol.*, 1914, **5**, No. 16, 1.

Cobaltous Hydroxide, $Co(OH)_2$, is obtained by precipitating a cobaltous salt with caustic potash in the absence of air. A blue precipitate is first obtained, and this, on boiling, is quickly converted into a rose-red coloured hydroxide. The blue precipitate was regarded as a basic salt, but Hantzsch [5] has shown that any basic salt present can be washed out without any change of colour occurring. Both the blue and rose varieties are hydroxides which differ only in the manner in which the water is combined. The blue compound is completely dehydrated at 170°, whereas the rose compound retains some water even after prolonged drying at 300°. The blue compound has therefore been given the formula CoO,H_2O and the rose compound $Co(OH)_2$. It absorbs oxygen from the air, the colour changing to brown, and dissolves in hot very concentrated potash, crystallising out on cooling in microscopic prisms.[6]

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[1] Hedvall, *Arkiv. Kem Min. Geol.*, 1914, **5**, No. 16, 1.

[2] *Ibid.*, *Zeit. anorg. Chem.*, 1915, **93**, 313; *ibid.*, 1916, **96**, 71.

[3] *Ibid.*, 1914, **86**, 296.

[4] *Ibid.*, 1915, **92**, 381.

[5] *Zeit. anorg. Chem.*, 1912, **73**, 304.

[6] De Schulten, *Compt. rend.*, 1889, **109**, 266. Compare Job., *ibid.*, 1907, **144**, 1044.

The cobaltous salts may be prepared by the action of acids on cobaltous hydroxide. They are the most stable of the cobalt salts, but undergo oxidation more readily than the corresponding compounds of nickel. In the anhydrous state they are deep violet or blue; in the hydrated condition, rose-red.

Cobaltic Oxide or Cobalt Sesquioxide, Co_2O_3, is a dark-brown powder, formed by gently igniting the nitrate.

Cobaltic Hydroxide, $Co(OH)_3$, is prepared by precipitating a cobalt salt with an alkaline hypochlorite solution. The composition of this precipitate depends on the conditions under which it has been produced, and frequently, especially when prepared in the cold, it contains more oxygen than corresponds to the formula Co_2O_3.[1] The sesquioxide is also obtained in a hydrated condition when an alkaline solution of cobalt sulphate is electrolysed,[2] or when a solution of the same salt is treated with potassium or ammonium persulphate.[3] It forms a brownish-black powder, which is decomposed by hydrochloric acid with evolution of chlorine, and by oxy-acids with evolution of oxygen.

The sesquioxide and its hydroxide act, therefore, as peroxides, but at the same time they possess weak basic properties, inasmuch as they dissolve in well-cooled acids, forming brownish-yellow solutions believed to contain cobaltic salts. One of the most stable of these compounds is a strongly coloured solution obtained by dissolving the hydroxide in acetic acid; this decomposes only when heated. The corresponding sulphate and some of its double salts have been isolated in the crystalline form.

Tricobalt Tetroxide or Cobalto-cobaltic Oxide, Co_3O_4.—This compound, which corresponds to the magnetic oxide of iron, is formed when one of the other oxides or the nitrate is heated to a temperature below 910° in the air;[4] thus obtained, it forms a black powder having a specific gravity of about 6·0. If a dry mixture of sal-ammoniac and cobalt oxalate or cobalt chloride be heated in the air, or in oxygen, this compound is obtained in hard, microscopic octahedra, which have a metallic lustre and are not magnetic. It is obtained in the hydrated state by the oxidation of moist cobaltous hydroxide in the air and also by warming cobaltous hydroxide with excess of potassium persulphate, washing and heating the product at 100° with dilute nitric acid.[1] When heated in the oxy-coal-gas flame it yields metallic cobalt, which becomes covered with a film of oxide as it cools.[2] The substance obtained by fusing one of the oxides with caustic potash, which was thought to be a potassium cobaltite,[3] $Co_9O_{16}K_2,3H_2O$, is probably cobalto-cobaltic oxide contaminated with potash,[4] or cobaltous potassium cobaltite.[5]

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[1] Carnot, *Compt. rend.*, 1889, **108**, 610; Schröder, *Journ. Chem. Soc.*, 1890, **58**, 1213; Hüttner, *Zeit. anorg. Chem.*, 1901, **27**, 81.

[2] Coehn and Gläser, *Zeit. anorg. Chem.*, 1903, **33**, 9.

[3] Mawrow, *Zeit. anorg. Chem.*, 1900, **24**, 263; Hüttner, *loc. cit.*

[4] See Burgstaller, *Chem. Zentr.*, 1912, ii., 1525.

Cobalt Dioxide, CoO_2, has not been obtained in the pure state. It appears, however, to be formed as a greenish-black precipitate when iodine and caustic soda are added to a solution of a cobaltous salt.[6] An oxide approaching this in composition is also formed by the action of a hypochlorite on a cobaltous salt, and probably brings about the well-known evolution of oxygen which occurs when bleaching powder solution is warmed with a small quantity of a cobalt salt (Vol. I., p. 245).[7]

According to McConnell and Hanes,[8] when cobaltous hydroxide is suspended in water and tested with hydrogen peroxide, and the liquid filtered, a strongly acid, colourless filtrate is obtained which appears to contain cobaltous acid, H_2CoO_3. If potassium bicarbonate be added to this filtrate, or if the oxidation be carried out in presence of potassium bicarbonate, a green solution is obtained, which probably contains potassium cobaltite, K_2CoO_3. On the other hand, Durrant[9] has failed to obtain evidence of the existence of this acid, and considers the green colour to be due to a derivative of cobaltic oxide to which he assigns the formula $[Co(KCO_3)_2]_2O$. Metzl[10] finds that the green precipitate is a mixture of cobaltous carbonate and cobalt cobaltite of the composition $CoCO_3,CoCoO_3$. Similar green compounds have been obtained with potassium salts of organic carboxylic acids and these may be formulated as derivatives of the radicle $>Co{\cdot}O{\cdot}Co<$. Sulphuric and sulphurous acids decolorise the green solution, but the colour reappears on neutralisation with potassium bicarbonate. Acetic acid does not decolorise the liquid, whilst, on warming with sulphuric acid, a pink solution of cobaltous sulphate is obtained.

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[1] Mawrow, *loc. cit.*

[2] Read, *Journ. Chem. Soc.*, 1894, **65**, 314.

[3] Schwarzenberg, *Annalen*, 1856, **97**, 212; Pebal, *ibid.*, 1856, **100**, 257; Mayer, *ibid.*, 1857, **101**, 266.

[4] McConnell and Hanes, *Journ. Chem. Soc.*, 1897, **71**, 584.

[5] Bellucci and Dominici, *Atti R. Accad. Lincei*, 1907, (5), **16**, i., 316.

[6] Vortmann, *Ber.*, 1891, **24**, 2744; Metzl, *Zeit. anorg. Chem.*, 1914, **86**, 358.

[7] McLeod, *British Assoc. Reports*, 1892, 669. But see Howell, *Journ. Chem. Soc.*, 1923, **123**, 65.

[8] *Loc. cit.*

[9] *Proc. Chem. Soc.*, 1896, **12**, 96, 244; *Journ. Chem. Soc.*, 1905, **87**, 1781; see also Job, *Compt. rend.*, 1898, **127**, 100.

[10] *Loc. cit.*

Barium Cobaltite, BaO,CoO_2, and *Barium Dicobaltite*, $BaO,2CoO_2$, are formed in black crystals when cobalt sesquioxide is fused with baryta and barium chloride.[1] These compounds evolve chlorine when treated with hydrochloric acid.

Magnesium Cobaltite, MgO,CoO_2, is formed as a deep garnet-red mass when magnesia is fused with cobalt sesquioxide in the electric furnace.[2]

Cobaltous Cobaltite, $CoO,2CoO_2,2H_2O$, is obtained by fusing cobaltous oxide with potassium peroxide, washing the cooled mass first with water and then with dilute sulphuric acid, and finally again with water, and drying over phosphoric oxide in a vacuum. It forms six-sided plates, and evolves chlorine when treated with hydrochloric acid.[3]

Cobalt and the Halogens.

586 *Cobaltous Fluoride*, CoF_2, is obtained by dissolving the oxide or carbonate in hydrofluoric acid;[4] on evaporation, rose-red crystals are deposited having the composition $CoF_2,2H_2O$: these are decomposed by boiling with the formation of a light red, insoluble oxyfluoride. The anhydrous fluoride is prepared by heating the chloride with ammonium fluoride in a current of hydrogen fluoride, and forms rose-coloured prisms slightly soluble in water.[5] It forms double salts with the alkali fluorides,[6] and absorbs dry ammonia to give the reddish-brown liquid hexammoniate, $CoF_2,6NH_3$. This loses ammonia in dry air giving the light pinkish-brown triammoniate, $CoF_2,3NH_3$, which loses all its ammonia at 40°.[7]

Cobaltic Fluoride, CoF_3, is obtained as a green powder when a saturated solution of cobaltous fluoride in 40 per cent. hydrofluoric acid is electrolysed in a platinum dish which acts as anode, a platinum wire being employed as cathode. It is decomposed by water with formation of cobaltic hydroxide.[8]

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[1] Rousseau, *Compt. rend.*, 1889, **109**, 64.

[2] Dufau, *ibid.*, 1896, **123**, 239.

[3] Hofmann and Hiendlmaier, *Ber.*, 1906, **39**, 2186. Compare Bellucci and Dominici, *Atti R. Accad. Lincei*, [5], 1907, **16**, i., 315.

[4] See Edminster and Cooper, *J. Amer. Chem. Soc.*, 1920, **42**, 2419.

[5] Poulenc, *Compt. rend.*, 1892, **114**, 1426.

[6] Compare Böhm, *Zeit. anorg. Chem.*, 1905, **43**, 326.

[7] Clark and Buckner, *J. Amer. Chem. Soc.*, 1922, **44**, 230.

[8] Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1905, [5], **14**, i., 464.

Cobalt Chloride, $CoCl_2$.—Powdered metallic cobalt takes fire when warmed in chlorine gas, forming blue, crystalline scales of the anhydrous chloride, which can be readily sublimed in a current of chlorine. They dissolve in alcohol, forming a blue solution, and on addition of water first become violet, and then rose-coloured. Cobalt chloride is obtained in aqueous solution by dissolving the carbonate, or one of the oxides, in hydrochloric acid; short, dark red, monoclinic prisms crystallise on cooling the concentrated warm solution; these possess the composition $CoCl_2,6H_2O$, and have a specific gravity of 1·84. When these crystals are allowed to stand over sulphuric acid at 50°, the rose-coloured dihydrate, $CoCl_2,2H_2O$, is formed, and when heated to 100° the deep violet monohydrate remains, which at 110–120° yields the blue, anhydrous chloride. A hydrate with $4H_2O$ has also been obtained.[1] A strong aqueous solution is rose-coloured, but becomes blue when it is heated, and when concentrated hydrochloric or sulphuric acid or alcohol is added. The rose colour is restored when the chloride of zinc, mercury, antimony, or tin is added to the solution which has been rendered blue by hydrochloric acid. These changes of colour have been attributed by some to the formation and decomposition of double salts or complex ions, by others to the hydration and dehydration of the cobalt salt.[2]

An unstable compound, $CoCl_2,HCl,3H_2O$, separates in blue crystals at −23° from a saturated solution of cobalt chloride in hydrochloric acid. A corresponding lithium compound is known which is also blue.[3] A compound with iodine trichloride, $CoCl_2,2ICl_3,8H_2O$, forms orange-red crystals.[4]

When anhydrous cobalt chloride is treated with ammonia the compound $CoCl_2,6NH_3$ is formed.[5] It is also obtained as dark rose-red crystals by passing ammonia into a saturated solution of cobalt chloride in methyl acetate.[6]

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[1] De Coninck, *Bull. Acad. roy. Belg.*, 1904, 1170.

[2] See Engel, *Bull. Soc. chim.*, 1891, **6**, 230; Potilitzine, *ibid.*, 264; Étard, *Compt. rend.*, 1891, **113**, 699; Charpy, *ibid.*, 704; Sabatier, *ibid.*, 1888, **107**, 42; Donnan and Bassett, *Journ. Chem. Soc.*, 1902, **81**, 939; Hartley, *ibid.*, 1903, **83**, 401; Moore, *Zeit. physikal. Chem.*, 1906, **55**, 641; Lewis, *ibid.*, **56**, 223; Benrath, *Zeit. anorg. Chem.*, 1907, **54**, 328; Denham, *Zeit. physikal. Chem.*, 1909, **65**, 641; Houstoun, *Proc. Roy. Soc. Edin.*, 1911, **31**, 521–558; Kotschubei, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1055.

[3] Chassevant, *Ann. Chim. Phys.*, 1893, [6], **30**, 5.

[4] Weinland and Schlegelmilch, *Zeit. anorg. Chem.*, 1902, **30**, 134.

[5] Ephraim, *Ber.*, 1912, **45**, 1322.

[6] Naumann, *ibid.*, 1909, **42**, 3789.

Sympathetic Inks.—If a dilute solution of the chloride be used as an ink, the writing is not visible when it is allowed to dry in the air, but on warming, the characters appear of a bright blue colour, disappearing again gradually on standing in the air, owing to the absorption of moisture.

From this property the cobalt salts have been employed for the manufacture of the so-called *sympathetic inks*; by this is understood any liquid the writing of which is invisible under ordinary conditions, but can be rendered apparent by some simple treatment. The first attempt at the preparation of such an ink depended upon the fact that a solution of lead acetate becomes black when treated with a decoction of orpiment in milk of lime. These two liquids were mentioned by Lemery in 1681 as "encres appellées sympathiques." In the treatise termed *The Key to unlock the Cabinet of the Secrets of Nature*, published in 1705, a method for preparing a sympathetic ink from certain bismuth ores is described. The peculiar properties of this ink were believed to be due to bismuth, but in 1744 Gessner proved that the cobalt in the ores was the active agent in the production of the ink. This property of the cobalt salts to change colour from rose to blue on loss of water has been applied also to the construction of floral hygrometers. Artificial flowers are prepared, the petals of which are tinted with cobalt salts. In damp weather the flower is pink, in dry weather violet or blue. This invention is a Parisian one, and dates from 1870.[1]

Cobalt Bromide, $CoBr_2$.—If bromine vapour is passed over metallic cobalt at a dark-red heat, a green fused mass of the anhydrous bromide is formed. By treating finely divided cobalt with bromine in dry ether, the compound $CoBr_2,(C_2H_5)_2O$ is obtained as a green substance which, on heating, yields the anhydrous cobalt bromide, $CoBr_2$.[2] The anhydrous salt absorbs water from the air, yielding a dark red liquid. This solution is obtained also by bringing cobalt, bromine, and water together; if the solution is allowed to stand over sulphuric acid, dark red prisms having the composition $CoBr_2,6H_2O$ are deposited, and these when heated to 100° give a purple mass containing $CoBr_2,2H_2O$, which at 130° yields the anhydrous bromide as an amorphous, green mass (Rammelsberg, Hartley). Several other hydrates are also known.[3] Cobalt bromide forms a hexammoniate,

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[1] See Vanino, *Arch. Pharm.*, 1917, 255, 81.

[2] Ducelliez and Raynaud, *Compt. rend.*, 1914, 158, 2002.

[3] Guareschi, *Atti R. Accad. Sci. Torino*, 1913, 48, 929.

$CoBr_2,6NH_3$, which is prepared in the same way as the corresponding chloride compound. It forms pale rose-red crystals which on heating to 120° decompose, yielding the diammoniate, $CoBr_2,2NH_3$, which is light blue in colour.[1]

Cobalt Iodide, CoI_2.—This substance is obtained in the anhydrous state by heating the metal in iodine vapour. It is also produced with evolution of heat when finely divided cobalt is gently warmed with water and iodine. The saturated solution is red up to 20°, and then passes through brown and olive to green at 35°. When poured into a saturated solution of magnesium chloride, a blue solution is formed (Étard). The hydrate, $CoI_2,6H_2O$, is dark red, whilst the tetrahydrate and the dihydrate are green, and the anhydrous salt resembles iodine. Double salts of this compound with other iodides are known.[2] Cobalt iodide gives two ammoniates, $CoI_2,6NH_3$ and $CoI_2,4NH_3$.

Cobalt Chlorate, $Co(ClO_3)_2$, is a somewhat unstable salt, which forms various hydrates.[3]

Cobalt Perchlorate has also been prepared.[4]

Cobalt Iodate, $Co(IO_3)_2$, crystallises from water in three forms: as anhydrous salt, as dihydrate, and as tetrahydrate.[5]

COBALT AND SULPHUR.

587 *Cobalt Monosulphide*, CoS, is obtained as a black, hydrated precipitate when a solution of a cobalt salt is mixed with ammonium sulphide. It dissolves in concentrated hydrochloric acid with evolution of sulphuretted hydrogen. The cold dilute acid dissolves it but slowly, whilst it is almost insoluble in dilute acetic acid. The monosulphide is found as an Indian mineral known as syepoorite, occurring in ancient schists in grains or veins of a yellowish steel-grey colour. It may be made artificially by heating cobalt sulphate with barium sulphide and sodium chloride.

When the monosulphide is mixed with sulphur and the mixture ignited in a current of hydrogen, the following sulphides are formed according to the temperature employed: CoS_2, Co_2S_3, CoS; and at a white heat, Co_2S (H. Rose).

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[1] Naumann, *loc. cit.*

[2] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 303; Mosnier, *Ann. Chim. Phys.*, 1897, [7], **12**, 374.

[3] Meusser, *Ber.*, 1902, **35**, 1417.

[4] Goldblum and Terlikowski, *Bull. Soc. chim.*, 1912, [4], **11**, 103, 146. Salvadori, *Gazz.*, 1912, **42**, i. 458.

[5] Meusser, *Ber.*, 1901, **34**, 2432.

Investigation of the freezing points of mixtures of cobalt and sulphur, containing up to 33·6 per cent. of the latter element, indicates the existence of the compounds Co_4S_3 and CoS.[1]

Cobalt pyrites or linnaeite, $(Co,Ni,Fe)_3S_4$, occurs at Bastnäs, near Riddarhyttan, at Müssen in Prussia, as well as at Mineral Hill in Maryland, and at Mine La Motte in Missouri. It forms steel-grey or tarnished copper-red regular octahedra, and occurs also in the massive state. It usually contains more or less nickel, as well as some iron and copper. It can be obtained artificially as a blackish-grey powder by heating a solution of a cobalt salt with potassium polysulphide to 160°.

A *polysulphide of cobalt*, which probably has the formula Co_2S_7, is obtained as a black precipitate when a solution of sodium monosulphide saturated with sulphur is added to one of cobalt chloride at the ordinary temperature.[2]

Cobaltous Sulphite, $CoSO_3,5H_2O$, is a pink, crystalline powder obtained by the action of sulphurous acid on cobaltous hydroxide. It forms double salts with the alkali sulphites.

Cobaltic Sulphite has not been isolated, but several double compounds, which are probably salts of a complex cobaltisulphurous acid, $H_3[Co(SO_3)_3]$, have been described.[3]

Cobaltous Sulphate, $CoSO_4,7H_2O$.—This salt occurs native as cobalt vitriol, or bieberite, in crystalline crusts. It is prepared artificially by dissolving the carbonate or oxide in dilute sulphuric acid, and crystallises in red prisms isomorphous with ferrous and nickel sulphate, which are unalterable in the air. It has a specific gravity of 1·924 (Schiff), possesses a weak, astringent, metallic taste, is easily soluble in water, but does not dissolve in alcohol. According to Mulder, 100 parts of water dissolve:

At	0°	10°	20°	30°	50°	70°	100°
$CoSO_4$	24·6	29·5	34·5	40·2	51·8	63·8	82·6.

When its solution is allowed to stand at 40–50°, monoclinic crystals having the composition $CoSO_4,6H_2O$ are formed, and these are isomorphous with the corresponding zinc salt. If a concentrated solution of cobalt sulphate is poured gently into sulphuric acid a peach-blossom coloured powder, $CoSO_4,4H_2O$, is deposited. The hydrate, $CoSO_4,H_2O$, is deposited when a solution of the salt is made slightly acid with sulphuric acid and evaporated.[1] All the hydrates lose their water on heating, but do not fuse, becoming opaque and of a rose-red colour (Proust). Cobalt sulphate forms numerous double salts. The double sulphates with ammonium and the alkali metals form a series all isomorphous with the corresponding ferrous and nickle double salts,[2] and also with the double selenates.[3] The double salt of cobalt sulphate with mercuric cyanide, $CoSO_4,Hg(CN)_2,10H_2O$, is interesting.[4] Cobalt sulphate has the power of absorbing notable quantities of nitric oxide, although the absorption is not accompanied by any change of colour.[5] It combines also with ammonia, giving a hexammoniate, $CoSO_4,6NH_3$.[6]

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[1] Friedrich, *Metallurgie*, 1908, 5, 212. Compare Bellucci, *Atti R. Accad. Lincei*, 1908, [5], 17, i., 18.

[2] Chesneau, *Compt. rend.*, 1896, 123, 1068.

[3] Berglund, *Ber.*, 1874, 7, 469.

Cobaltic Sulphate, $Co_2(SO_4)_3,18H_2O$, is deposited in blue, silky needles, when a cooled acid solution of cobaltous sulphate is electrolysed in a divided cell. It dissolves in water, forming a blue solution which rapidly decomposes to cobaltous sulphate with evolution of oxygen. The crystals decompose on exposure to the air, finally becoming pink. It forms a greenish-blue solution in dilute sulphuric acid, which gives a black precipitate with alkalis and is rapidly decomposed by reducing agents. With hydrochloric acid, chlorine is evolved.[7]

Cobaltic Ammonium Alum, $(NH_4)_2SO_4,Co_2(SO_4)_3,24H_2O$, is obtained by adding ammonium sulphate to an acid solution of cobaltous sulphate and passing a weak current. It forms blue octahedra and is stable when dry, but decomposes in solution, ozonised oxygen being liberated. The potassium, rubidium, and cæsium alums have been obtained in a similar manner.[8]

Cobalt and Nitrogen.

588 *Cobalt Nitride*, Co_2N, is obtained as a dull grey powder[9] when metallic cobalt is heated in ammonia at about 470°. It is soluble in hydrochloric and sulphuric acids, and loses its nitrogen when heated to 600°. The nitride, Co_3N_2, is obtained by passing a mixture of cobaltous oxide and anhydrous cobalt

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[1] Lescœur, *Ann. Chim. Phys.*, 1895, [7], **4**, 213.

[2] Tutton, *Phil. Trans.*, 1915, [*A*], 210, 1.

[3] *Ibid.*, *Proc. Roy. Soc.*, 1919, [*A*], **96**, 156.

[4] Scagliarini and Bonini, *Gazz.*, 1920, **50**, ii., 114.

[5] Hüfner, *Zeit. physikal. Chem.*, 1907, **59**, 416.

[6] See Ephraim, *Ber.*, 1912, **45**, 1322.

[7] Marshall, *Journ. Chem. Soc.*, 1891, **59**, 760.

[8] *Idem.*, *ibid.*; Howe and O'Neal, *J. Amer. Chem. Soc.*, 1898, **20**, 759.

[9] Beilby and Henderson, *Journ. Chem. Soc.*, 1901, **79**, 1251.

cyanide between the poles of an electric arc in an atmosphere of nitrogen. It burns in oxygen, yielding cobaltous oxide and nitrogen peroxide, and is soluble in hydrochloric and nitric acids.[1]

Cobalt Azoimide, or *Azide*, $Co(N_3)_2$, together with a *basic azoimide*, $N_3Co(OH)$, is obtained by the action of aqueous azoimide on a cobalt salt, as a violet powder.[2] It has been prepared in the pure state by shaking the finely divided dry basic azide or cobalt carbonate with an ethereal solution of azoimide.[3] It is extremely explosive, even gentle rubbing causing a violent detonation. It is soluble in water, but the solution is rapidly hydrolysed. Double compounds with potassium and ammonium azoimides have also been obtained.

Nitro-cobalt, $Co_2(NO_2)$, is formed when diluted nitrogen peroxide is passed over reduced metallic cobalt. It is a black mass, which is vigorously decomposed by water, and explodes when mixed with combustible matter.[4]

Cobalt Nitrite.—Neither cobaltous nor cobaltic nitrite has been prepared in the solid state.[5] The double potassium salt described below differs in many of its properties from an ordinary nitrite, and is probably, like the cobalticyanides and the cobaltammine salts, a derivative of a complex acid.[6]

Potassium Cobaltinitrite, $K_3[Co(NO_2)_6]$, which is known as Fischer's salt after its discoverer,[7] is obtained as a yellow precipitate when the solution of a cobaltous salt, acidified with acetic acid, is mixed with a solution of potassium nitrite:

$$CoCl_2+5KNO_2+2HNO_2=K_3Co(NO_2)_6+2KCl+NO+H_2O.$$

As this salt is somewhat soluble in water, it is best to wash it with a solution of potassium acetate, and then with 80 per cent. alcohol. It is also produced by passing nitrous fumes into a suspension of cobalt carbonate in a solution of potassium carbonate or nitrite. Cobalt yellow, as this compound is also termed, is a bright yellow powder consisting of microscopic pyramids, or of four- or six-sided stellated forms. According to Sadtler,[8] the salt is usually anhydrous; it can, however, be obtained, according to the concentration of the solution, with from one to four molecules of water, and its colour then varies from a bright yellow to a dark greenish-yellow. It is decomposed by nitric and hydrochloric acids, but only when heated. Caustic potash solution attacks it with difficulty. Caustic soda or baryta water, on the other hand, decomposes it readily, on gently warming, with precipitation of the brown hydroxide. The salt suspended in water is only slowly attacked by sulphuretted hydrogen, but ammonium sulphide instantly precipitates black cobalt sulphide. The fact that cobalt is precipitated by a solution of potassium nitrite, acidified with acetic acid, is employed in the analytical separation of cobalt from nickel and other metals.[1]

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[1] Vournasos, *Compt. rend.*, 1919, **168**, 889.

[2] Curtius and Rissom, *J. pr. Chem.*, 1898, [2], **58**, 261.

[3] Wöhler and Martin, *Ber.*, 1917, **50**, 586; *Zeit. angew. Chem.*, 1917, **30**, i. 33.

[4] Sabatier and Senderens, *Bull. Soc. chim.*, 1893, [3], **9**, 669.

[5] See Suzuki, *Journ. Chem. Soc.*, 1910, **97**, 726.

[6] Hofmann and Burger, *Ber.*, 1907, **40**, 3298; Rosenheim and Garfunkel, *ibid.*, 1911, **44**, 1865.

[7] *Pogg. Ann.*, 1848, **74**, 124.

[8] *Amer. J. Sci.*, [2], 1870, **49**, 189.

Sodium cobaltinitrite is made in a similar way, but owing to its solubility in water it is precipitated from the aqueous solution by addition of alcohol. A solution of this salt is used for testing for potassium,[2] a yellow precipitate of the insoluble potassium salt being obtained. The corresponding compounds of rubidium and cæsium are distinguished by being only one-tenth as soluble as their platinichlorides.[3] The corresponding ammonium, silver, thallium, lead, and barium compounds can be prepared by double decomposition of a soluble salt with the sodium compound.

If a solution of cobalt chloride be precipitated with potassium nitrite without addition of acid, a yellow, hydrated precipitate of potassium cobaltous nitrite, $2KNO_2,Co(NO_2)_2$, is obtained, soluble in hot water and yielding a red solution.[4]

Cobalt Nitrate, $Co(NO_3)_2,6H_2O$.—This substance is obtained by dissolving the oxides, hydroxides, or carbonate in nitric acid, and generally forms an indistinctly pink, crystalline mass. It may be obtained by slow evaporation in monoclinic prisms, having a specific gravity of 1·83 and not undergoing change in dry air. It begins to melt below 100°, and when more strongly heated the violet liquid becomes thick and green; then it begins to boil, giving off nitrous fumes, and the black oxide is left. Anhydrous cobalt nitrate is a slightly pink powder, which begins to decompose at 100–105°.[5] Hydrates with nine and three molecules of water also exist.[1] Cobalt nitrate gives a hexammoniate. It forms a double nitrate with bismuth of the composition $3Co(NO_3)_2,2Bi(NO_3)_3,24H_2O$,[2] and a double salt with mercuric cyanide, $Co(NO_3)_2Hg(CN)_2,6H_2O$.[3]

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[1] Funk, *Zeit. anal. Chem.*, 1907, **46**, 1.

[2] See Adie and Wood, *Journ. Chem. Soc.*, 1900, **77**, 1076; Biilmann, *Zeit. anal. Chem.*, 1900, **39**, 284; Cunningham and Perkin, *Journ. Chem. Soc.*, 1909, **95**, 1562; Burgess and Kamm, *J. Amer. Chem. Soc.*, 1912, **34**, 652.

[3] Rosenbladt, *Ber.*, 1886, **19**, 2531.

[4] Erdmann, *J. pr. Chem.*, 1866, **97**, 385.

[5] Guntz and Martin, *Bull. Soc. chim.*, 1909, [4], **5**, 1004.

Ammoniacal Cobalt Compounds or Cobaltammine Salts.

589 In 1799, Tassaert[4] observed that a solution of a cobalt salt in ammonia assumes a brown colour on exposure to the air, and that this changes on boiling to a wine-red, whilst Thénard,[5] in 1802, stated that these changes were brought about by an absorption of oxygen. This latter observation was confirmed by Proust, who found that, on evaporating the solution, black cobaltic oxide separates out. The compounds which are thus formed have attracted the attention of many chemists,[6] and a very large number of these cobaltammine salts have been prepared, as well as compounds with organic substituted ammonias such as pyridine, quinoline, ethylene diamine, etc. A general account of this class of substances has been given on p. 1087, and only one or two typical compounds of each class are here described.

(1) *Hexammine Salts* (*Luteo-salts*), $[(NH_3)_6Co]X_3$, where X is a univalent acid radicle, are formed when dilute solutions of cobaltous salts, containing a large amount of ammonia and ammonium chloride, are exposed to the oxidising action of the air; they are produced also by the action of ammonia on many of the salts containing five molecules of ammonia.

The compound *Hexammine-cobaltic Chloride* (*Luteocobaltic Chloride*), $[(NH_3)_6Co]Cl_3$, is obtained when an ammoniacal cobalt chloride solution is allowed to stand for some time, especially in the presence of sal-ammoniac. The formation of the salt is facilitated by the addition of oxidising substances such as lead dioxide, bromine, etc. (Braun, Mills). It crystallises in reddish-yellow, monoclinic prisms or pyramids, which dissolve slowly in cold but readily in hot water. It forms a sparingly soluble platinichloride.

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[1] Funk, *Zeit. anorg. Chem.*, 1899, **20**, 407.

[2] Urbain and Lacombe, *Compt. rend.*, 1903, **137**, 568.

[3] Scagliarini and Bonini, *Gazz.*, 1920, **50**, ii. 114.

[4] *Ann. Chim.*, 1798, **28**, 95.

[5] *Ibid.*, 1802, **42**, 210.

[6] A history of these compounds will be found in *Untersuchungen der Ammoniakalische Kobalt Verbindungen*, by Fr. Rose, Heidelberg, 1871. For more recent work, see the references on p. 1348.

(2) *Pentammine Salts* form two distinct classes of compounds, the *aquo-pentammine salts (roseo-salts)*, $[H_2O(NH_3)_5Co]X_3$, and the *acido-pentammine salts*, $[X(NH_3)_5Co]X_2$. The latter salts have been distinguished by different names according to the nature of the acid group in the complex radicle, the salts of the various series usually possessing characteristic colours.

The aquopentammine salts, which are pink, lose water when heated with acids, forming derivatives of the second class, whilst the latter are reconverted into aquopentammine salts by boiling or standing with water. By the action of ammonia on the aquopentammine salts the so-called hydroxypentamminecobalt salts are obtained, thus: $[(H_2O)(NH_3)_5Co]X_3 + NH_3 = [(OH)(NH_3)_5Co]X_2 + NH_4X$.

Chloro-pentammine-cobaltic Chloride (Chloropurpureo-cobaltic Chloride), $[Cl(NH_3)_5Co]Cl_2$, is obtained by boiling a solution of roseo-cobaltic chloride; it falls as a red precipitate, soluble at 10° in 287 parts of water, and crystallising in tetragonal prisms. With platinichloric acid, it forms the salt, $[Cl(NH_3)_5Co]PtCl_6$, which is almost insoluble in cold water, and separates as a brownish-red powder. If the chloride be triturated with strong sulphuric acid, a solution of *chloro-pentammine-cobaltic sulphate*, $[Cl(NH_3)_5Co]SO_4$, is formed, and if nitric acid be added to this solution fine, red, microscopic crystals of *chloro-pentammine-cobaltic nitrate*, $[Cl(NH_3)_5Co](NO_3)_2$, are thrown down, the solution of which is not precipitated by silver nitrate.

(3) *Tetrammine Salts* are analogous to the pentammine salts, but the complex radicle contains only four molecules of ammonia and two other groups, which may be water or the hydroxy-group or a univalent acid radicle.

Dichloro-tetrammine-cobaltic Chloride (Praseo-cobaltic Chloride), $[Cl_2(NH_3)_4Co]Cl,H_2O$, is usually formed together with the other cobaltammine chlorides. It crystallises in small, glistening needles which possess an emerald green colour, whence the term praseo is derived. These dissolve in water, yielding a green solution which soon becomes red, and undergoes decomposition on boiling. If fusco-cobaltic chloride, $Co(NH_3)_4Cl_2(OH)$, be warmed with dilute hydrochloric acid, a deep violet solution is obtained, and this on cooling deposits small violet octahedra which possess the same composition as the green salt, and pass into the latter when dissolved in concentrated sulphuric acid, to which hydrochloric acid is gradually added.

Dinitrito-tetrammine-cobaltic Sulphate (Croceo-cobaltic Sulphate),

$[(NO_2)_2(NH_3)_4Co]_2SO_4$, is formed when a mixture of solutions of cobalt sulphate and potassium nitrite, saturated with ammonia, is exposed to the air. It is deposited in orange-yellow crystals together with green cobaltic hydroxide. The mixture is filtered and the residue dissolved in hot dilute nitric acid, and from this solution the sulphate is obtained on cooling in the form of yellow tetragonal tablets. Large wine-red crystals are also obtained from dilute solutions. It is slightly soluble in boiling water.

(4) *Triammine compounds* are formed from the tetrammine salts by loss of ammonia. They possess the general formula $[X_3(NH_3)_3Co]$, and are non-electrolytes in aqueous solution. *Aquotriammine salts* are also known, with one or more of the acid groups outside the complex radicle, which contains one molecule of water for each acid group replaced.

Trinitrito-triammine-cobalt, $[(NO_2)_3(NH_3)_3Co]$, is prepared by acting on cobaltous chloride solution with ammonia and potassium nitrite (Erdmann), and by the action of ammonium nitrite on cobaltous chloride in presence of acetic acid (Gibbs).

Triaquo-triammine-cobaltic Chloride, $[(H_2O)_3(NH_3)_3Co]Cl_3$, is prepared from trinitrito-triammine-cobalt by treating first with dilute acetic acid and then with hydrochloric acid at 0°.

(5) *Diammine salts* have been very slightly investigated.

Potassium Tetranitrito-diammine cobaltite (Erdmann's salt) $[(NO_2)_4(NH_3)_2Co]K$, is obtained by adding ammonium chloride and potassium nitrite to a solution of cobaltous chloride and gently warming. It forms yellow, rhombic crystals.

In addition to the classes of compounds already described, several series of substances have been prepared which Werner terms multi-nuclear ammoniacal compounds.[1] Examples of these are the *oxycobaltammines*, $\{O_2[Co_2(NH_3)_5]_2\}X_4$, and the series $\{NH[Co(OH)_2(NH_3)_4]_2\}X_4$, and $Co\{Co(OH)_2(NH_3)_4]_3X_6$.

The relations between the various complex cobalt compounds just described have been successfully interpreted by means of Werner's theory of principal and supplementary valencies (see p. 36). The further development of this theory has suggested the possibility of the occurrence of *cis*- and *trans*-isomerism and of optical isomerism—deductions that have been fully verified by the preparation of substances of this description. These deductions are based on the view that the six groups associated with the cobalt atom are arranged round this central atom in the positions corresponding with the angles of an octahedron.[1]

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[1] Werner, *Ber.*, 1907, **40**, 66, 2103.

COBALT WITH PHOSPHORUS, ARSENIC, AND ANTIMONY.

590 *Phosphides of Cobalt.*—When pieces of phosphorus are thrown on to heated cobalt a bluish-white, brittle mass with a metallic lustre is formed. This tarnishes on exposure to air, melts at a lower temperature than cobalt, and contains 6 per cent. of phosphorus. On heating, it burns, with formation of a dark blue glass (Pelletier). When cobalt reduced in hydrogen is heated to dark redness in the vapour of phosphorus, a light grey mass with a metallic lustre is formed, containing 28·4 per cent. of phosphorus (Schrötter), and corresponding nearly to the formula Co_4P_3. A compound, Co_3P_2, is also formed as a black powder by igniting a normal phosphate in a current of hydrogen.

The *phosphide*, Co_2P, is obtained when cobalt formed by reduction of the oxide or oxalate is heated to redness in the vapour of phosphorus trichloride, tribromide or di-iodide,[2] and a substance of this composition is also produced in grey crystals when finely divided cobalt is heated with a copper phosphide in the electric furnace.[3] The existence of this compound is indicated by the occurrence of a maximum on the freezing-point curve for mixtures of phosphorus and cobalt.[4] Another compound, Co_3P_3, is obtained as a black, metallic mass by heating cobalt chloride to dull redness in phosphorus vapour.[5]

Cobalt Arsenide, $CoAs_3$, occurs as skutterudite near Modum, in Norway, crystallised in octahedral forms as well as in the massive state. It possesses a colour from tin-white to a pale lead-grey, and usually contains small quantities of iron and sulphur. Smaltite or tin-white cobalt, $CoAs_2$, usually contains varying quantities of iron and nickel, and occurs in tin-white octahedral forms as well as in the massive state in the Erzgebirge. Cobaltite, cobalt glance, or bright white cobalt, $CoAs_2,CoS_2$ or CoAsS, crystallises in the regular system, usually in pyramid octahedra and their combinations, and a portion of the cobalt is generally replaced by iron. It has a silver-white colour inclining to red, and occurs in Sweden, in Westphalia, and in the Bottolack Mine near St. Just in Cornwall. Other arsenides, Co_3As_2, CoAs, and Co_2As_3, have been prepared.[1]

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[1] For a summary of Werner's later work, on both the theoretical and practical sides, see *Chemical Society's Annual Reports*, 1911, **8**, 77; also Werner, *Ber.*, 1912, **45**, 121.

[2] Granger, *Compt. rend.*, 1896, **123**, 176.

[3] Maronneau, *ibid.*, 1900, **130**, 656.

[4] Schemtschuschny and Schepeleff, *Zeit. anorg. Chem.*, 1909, **64**, 245.

[5] Granger, *Compt. rend.*, 1896, **122**, 1484.

Cobalt antimonide, CoSb, and *cobalt di-antimonide*, $CoSb_2$, are crystalline powders melting about 1200° and 700° respectively.[2]

Phosphates and Arsenates of Cobalt.—The normal and monohydrogen cobalt salts of the different modifications of phosphoric acid are rose-red or violet-blue, insoluble compounds. The di-hydrogen-orthophosphate is easily soluble in water and forms a gummy mass. The arsenates are similar bodies; the normal arsenate, $Co_3(AsO_4)_2,8H_2O$, occurs native as cobalt bloom or erythrite, in violet, monoclinic needles isomorphous with vivianite, or in earthy masses. *Zaffre* is an impure basic arsenate obtained by roasting cobalt glance free from iron, or by dissolving the ore in nitric acid and precipitating with soda. It is used for painting on porcelain.

Three insoluble ammoniacal arsenates have been obtained by the action of arsenic acid on solutions of cobalt salts in the presence of ammonia and ammonium salts. These compounds have the formulæ $Co_3(AsO_4)_2,NH_3,7H_2O$, $Co_3(AsO_4)_2,2NH_3,6H_2O$, and $Co_3(AsO_4)_2,3NH_3,5H_2O$, and may be considered as the normal arsenate in which the water of crystallisation is partially replaced by ammonia.[3]

Cobalt and Carbon.

591 *Cobalt Carbide* has not been isolated. Carbon dissolves in molten cobalt and the solubility curve indicates the existence of a compound, Co_3C, analogous to cementite, Fe_3C, but it decomposes so rapidly on cooling that it cannot be detected even in the quenched metal.[4]

Cobaltous Carbonate.—The normal salt, $CoCO_3$, is obtained as a bright-red powder, consisting of microscopic rhombohedra, by heating cobalt chloride to 140° with a solution of sodium bicarbonate saturated with carbon dioxide. The hydrated salt, $CoCO_3,6H_2O$, is formed by allowing mixed solutions of cobalt nitrate and sodium bicarbonate, saturated with carbon dioxide, to stand at a low temperature until the amorphous precipitate which is first formed becomes crystalline; the dry salt is converted into the anhydrous salt on warming. When a solution of a cobalt salt is precipitated with normal or acid sodium carbonate, bluish or violet basic cobalt carbonates of varying composition are thrown down.[1] Cobalt carbonate forms a pink double salt with potassium carbonate,[2] and a bright reddish-purple one with sodium carbonate.[3] They have the formula $M_2CO_3,CoCO_3,4H_2O$.

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[1] Ducelliez, *Compt. rend.*, 1908, **147**, 424.

[3] *Ibid.*, 1048.

[2] Ducru, *ibid.*, 1900, **131**, 675.

[4] Ruff and Keilig, *Zeit. anorg. Chem.*, 1914, **88**, 410. See also Arnold and Read, *Proc. Inst. Mech. Eng.*, 1915, 247.

Cobalt Tetracarbonyl, $Co_2(CO)_8$, is obtained by heating cobalt in a nickel-steel vessel at about 150° with carbon monoxide under a pressure of not less than 30 atmospheres.[4] In this way, fine, orange-coloured crystals of cobalt tetracarbonyl are obtained, which are best kept in a sealed glass tube in an atmosphere of hydrogen or carbon monoxide. If left in contact with the air, the substance decomposes, yielding a basic cobalt carbonate. Cobalt tetracarbonyl is insoluble in water, but dissolves more or less in organic solvents, such as carbon disulphide, ether, or alcohol. The double molecular formula, $Co_2(CO)_8$, is established by cryoscopic determinations. The pure crystals melt at 51° without decomposition, but this sets in immediately thereafter. At 60°, decomposition is fairly rapid and results in the formation of

Cobalt Tricarbonyl, $Co(CO)_3$.—This compound crystallises from benzene in jet-black crystals, which may be decomposed with bromine water for the purpose of analysis. It is very liable to change in air, and is sparingly soluble in the common solvents.

Cobalt Nitroso-tricarbonyl, $Co(CO)_3,NO$.—Nitric oxide reacts with cobalt tetracarbonyl, slowly at ordinary temperature but instantaneously at 40°, partly decomposing it into the tricarbonyl and carbon monoxide and partly converting it into the nitroso-tricarbonyl:[5]

$$Co(CO)_4 + NO = Co(CO)_3,NO + CO.$$

Cobalt nitroso-tricarbonyl is a cherry-red mobile liquid of density 1·5126 at 14°; melting point − 1·05°; boiling point 78·6°. It may be distilled with only slight decomposition at

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[1] Compare Meigen, *Journ. Chem. Soc.*, 1905, **88**, ii, 454; Nanty, *Ann. Chim. Phys.*, 1912, [8], **27**, 5; 1913, [8], **28**, 77.

[2] Wood and Jones, *Proc. Camb. Phil. Soc.*, 1907, **14**, 171; Applebey and Lane, *Journ. Chem. Soc.*, 1918, **113**, 609.

[3] Applebey and Lane, *loc. cit.*

[4] Mond, Hirtz, and Cowap, *Journ. Chem. Soc.*, 1910, **97**, 798.

[5] Mond and Wallis, *Journ. Chem. Soc.*, 1921, **121**, 29.

50°—60° in a current of inert gas, but above this temperature it decomposes into the tricarbonyl and nitric oxide. It is insoluble in water but miscible in all proportions with alcohol, ether, benzene or chloroform.

Cobaltous Cyanide, $Co(CN)_2,3H_2O$, is a reddish precipitate obtained when solutions of potassium cyanide and a cobalt salt are mixed. It dissolves easily in excess of the precipitant, probably forming a solution of potassium cobaltocyanide. If the solution is treated with dilute hydrochloric acid, cobaltous cyanide is again precipitated, but if the solution is previously warmed this does not occur, inasmuch as the more stable potassium cobalticyanide is formed (see below).

The cobaltocyanides and cobalticyanides are analogous in composition to the ferro- and ferri-cyanides (p. 1302), and may be regarded as salts of a complex radicle containing cobalt.[1] The cobalt is not precipitated by the usual reagents, but the compounds, especially the cobaltocyanides, are not so stable as the corresponding iron compounds.

Potassium Cobaltocyanide, K_4CoCy_6, is a deep amethyst-coloured, crystalline powder, which is obtained by dissolving cobaltous cyanide in potassium cyanide at a low temperature and precipitating with alcohol.[1] The formation of this salt is also indicated by the change in electrical conductivity as potassium cyanide solution is gradually added to cobalt chloride solution.[2]

Potassium Cobalticyanide, K_3CoCy_6, is formed when an excess of potassium cyanide is added to a solution of a cobalt salt, together with a little acetic acid or hydrochloric acid, and the liquid well boiled:

$$6KCy + 2CoCy_2 + 2HCy = 2K_3CoCy_6 + H_2.$$

When a solution of potassium cobaltocyanide is rapidly oxidised by atmospheric oxygen, it is converted into the cobalticyanide, and twice as much oxygen is absorbed as is required by the equation:

$$2K_4CoCy_6 + H_2O + O = 2K_3CoCy_6 + 2KOH.$$

At the end of the reaction hydrogen peroxide is found in the solution in an amount corresponding to the whole of the absorbed oxygen. On the other hand, when a solution of the cobaltocyanide is boiled, hydrogen is evolved equal in volume to the oxygen actually absorbed by the above oxidation. Manchot and Herzog,[1] therefore, consider that the oxidation of potassium cobaltocyanide in solution is effected by the water, the absorbed oxygen uniting with the hydrogen liberated to form hydrogen peroxide.

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[1] See Descamps, *Ann. Chim. Phys.*, [5], 1881, 24, 193.

[2] Rossi, *Gazz.*, 1915, 45, i, 6.

This salt crystallises in bright yellow crystals isomorphous with potassium ferricyanide.[2] Copper sulphate yields a blue, and silver nitrate a white precipitate, the salts $Cu_3(CoCy_6)_2$ and Ag_3CoCy_6 being formed. *Ferrous cobalticyanide*, $Fe_3(CoCy_6)_2$, is a white precipitate, whilst *cobaltous cobalticyanide*, $Co_3(CoCy_6)_2,14H_2O$, is a pink precipitate which becomes anhydrous and blue when heated to 200°. Cobalticyanides of other metals[3] and also of organic bases[4] have been described. When the copper salt is decomposed by sulphuretted hydrogen, *cobalticyanic acid*, H_3CoCy_6, is formed, and this is deposited in colourless, silky needles on evaporating the solution. It is deliquescent, has a strongly acid taste and reaction, and is not attacked even by strong nitric acid.

COBALT AND SILICON, ALUMINIUM, AND ZINC.

592 *Cobalt Silicides.*—The compound Co_2Si is produced when cobalt is heated with silicon in the electric furnace, or at 1200–1300° in silicon tetrachloride vapour, and forms grey, metallic crystals of specific gravity 7·28.[5] By heating cobalt in the electric furnace with copper silicide the *monosilicide*, CoSi, is formed, whilst with excess of silicon or a mixture of copper silicide and silicon, the *disilicide*, $CoSi_2$, is obtained.[6] Other silicides are also known.[7]

Silicates of Cobalt. Smalt.—The silicates of cobalt do not occur as minerals in nature. Although certain specimens of ancient Egyptian glass have been found to be coloured blue by cobalt, the direct application of the ores of cobalt for this purpose appears to date from the sixteenth century. Smalt is a potash glass coloured an intense blue by cobalt oxide. Up to the middle of the nineteenth century smalt was largely used for colouring starch, paper, etc., but the introduction of artificial ultramarine has diminished the demand for cobalt blue.

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[1] *Ber.*, 1900, **33**, 1742. See also Moore, *Chem. News*, 1893, **68**, 295.

[2] Gmelin, *Handbuch Org. Chem.*, **1**, 397.

[3] Miller and Mathews, *J. Amer. Chem. Soc.*, 1900, **22**, 62.

[4] Wagener and Tollens, *Ber.*, 1906, **39**, 410.

[5] Vigouroux, *Compt. rend.*, 1895, **121**, 686; 1906, **142**, 635.

[6] Lebeau, *Ann. Chim. Phys.*, 1902, **27**, 271.

[7] Jenge, *Zeit. anorg. Chem.*, 1921, **118**, 105.

For the preparation of smalt, the ore, such as speiss-cobalt or cobalt glance, free as far as possible from iron and sulphur, is first carefully roasted so that the cobalt mainly is oxidised, whilst nickel, iron, copper, and bismuth remain for the most part unaltered together with sufficient arsenic to combine with them and allow them to separate out as an insoluble speiss when the mixture is melted with glass. The roasted ore is then fused with a mixture of quartz sand and potashes, the fusion being effected in large earthen pots, arranged in a furnace similar to that employed for the manufacture of plate glass. The arsenides of nickel and iron sink to the bottom of the pot and the glass is ladled out into cold water. The blue glass is then ground with water to an impalpable powder under granite stones.

Smalt varies in composition according to the differences in the ores, and the proportion of sand and potashes employed. Thus the amount of silica varies between 56 and 70 per cent., that of potash between 12 and 22, and that of cobalt between 6 and 16 per cent. In addition, smalt contains small quantities of alumina, ferric oxide, and frequently also lime and oxide of lead; the commoner varieties likewise contain oxide of nickel. Smalt has the advantage as a paint over ultramarine that its colour is not destroyed by the action of acids.

A number of other coloured substances containing cobalt are made by heating the oxide with other metallic oxides (p. 1333).

DETECTION AND ESTIMATION OF COBALT.

593 This metal is characterised by the fine blue colour which its compounds impart to the borax bead. If a cobalt compound be reduced on a carbonised match, the metal is obtained in shining, white, magnetic particles; these dissolve in hydrochloric acid, forming a rose-red solution, which becomes blue on evaporation.

Cobalt chloride imparts to the non-luminous gas flame an evanescent rose-red colour, but this does not give any characteristic spectrum. The spark spectrum of the chloride contains a large number of bright lines, and the metal also gives a spectrum consisting of a large number of bright lines of which the following in the blue are the most characteristic (Thalén); 4868, 4840, 4815, 4793, 4780.

Solutions of cobalt salts give with ammonium sulphide a black precipitate of the sulphide which is insoluble in acetic and dilute hydrochloric acids. With ammonium thiocyanate, they yield a blue coloration, and if this solution be shaken with a mixture of amyl alcohol and ether and then allowed to stand, the latter separate on the top as an intensely blue layer.[1] Addition of acetic acid and potassium nitrite to a solution containing cobalt yields a yellow precipitate of potassium cobalti-nitrite. α-nitroso-β-naphthol gives a red precipitate with solutions of cobalt salts acidified with acetic acid.[2]

The separation of nickel and cobalt is discussed under nickel (p. 1385).

Cobalt may be estimated electrolytically in the same manner as nickel. It may also be accurately estimated by precipitation with α-nitroso-β-naphthol; the precipitate is ignited with a little oxalic acid to the oxide, reduced in a stream of hydrogen, and weighed as metal. Cobalt may also be precipitated as the oxide (by alkaline hypobromite) or sulphide, which is similarly ignited, reduced in hydrogen, and weighed as metal.

The Atomic Weight of cobalt, like that of nickel, has been frequently determined. Among the earlier determinations may be mentioned those of Rothhoff,[3] Schneider,[4] Marignac,[5] Gibbs,[6] Dumas,[7] Russell,[8] Zimmermann,[9] and Winkler.[10] In an investigation by Hempel and Thiele[11] the reduction of tricobalt tetroxide gave the number 58·97, and the analysis of the chloride 58·89. Richards and Baxter[12] determined the ratios of cobalt bromide to silver bromide and to silver, and as the mean of a large number of experiments obtained the number 58·99. They determined also the weight of cobalt obtained by the reduction of cobaltous oxide, chloride, and bromide by heating in hydrogen, and obtained numbers between 58·93 and 59·06.

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[1] See Powell, *J. Soc. Chem. Ind.*, 1917, **36**, 273.

[2] Ilinski and Knorre, *Ber.*, 1885, **18**, 699; Chapin, *J. Amer. Chem. Soc.*, 1907, **29**, 1929; Atack, *J. Soc. Chem. Ind.*, 1915, **34**, 641.

[3] *Pogg. Ann.*, 1826, **8**, 185.

[4] *Ibid.*, 1857, **101**, 387.

[5] *Arch. Sci. Phys. Nat.*, 1858, [2], **1**, 373.

[6] *Amer. J. Sci.*, 1858, [2], **25**, 438.

[7] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.

[8] *Journ. Chem. Soc.*, 1863, **16**, 51; *Chem. News*, 1869, **20**, 20.

[9] *Annalen*, 1885, **232**, 324.

[10] *Zeit. anal. Chem.*, 1867, **6**, 22; *Zeit. anorg. Chem.*, 1895, **8**, 1,

[11] *Ibid.*, 1896, **11**, 73.

[12] *Ibid.*, 1898, **16**, 326; 1899, **21**, 250; 1899, **22**, 221. Compare Winkler, *ibid.*, 1898, **17**, 236.

More recently, from the ratios of cobalt chloride to silver and to silver chloride, Baxter and Coffin[1] found the number 58·99. The value at present (1922) adopted is 58·97.

The atomic weight of cobalt is higher than that of nickel. Chemical analogies require that cobalt should precede nickel in the periodic system (p. 69), and the atomic numbers of the elements are in this order (see p. 74).

NICKEL. Ni = 58·68. At. No. 28.

594 The first mention of an ore of this metal is found in the writings of Hiarni in 1694, the name of kupfer-nickel, signifying false copper, being given to it because, whilst possessing the colour of a copper ore, this latter metal could not be extracted from it. In spite of the failure, the ore was long supposed to contain copper, but after the discovery of cobalt many believed that this metal was contained in kupfer-nickel.[2] In 1751, Cronstedt published in the *Transactions* of the Stockholm Academy an investigation upon an ore which was obtained from the mines of Helsingland. This gave a green vitriol, which imparted a brown and not a blue colour to glass, and yielded a hard, brittle metal. In 1754, he stated that a semi-metal occurred most abundantly in kupfer-nickel, and therefore he proposed to give to it the name of nickel. He likewise showed that the speiss formed in the preparation of smalt consisted to a large extent of nickel, and was not, as had been believed, a burnt cobalt which had lost its spirit. Cronstedt's views did not find general acceptance; but in 1774 Bergman's research on nickel made its appearance, and in this he showed that the nickel which Cronstedt had obtained only in the impure state was in reality a new metal.

Nickel almost always occurs in nature together with cobalt, and occurs in niccolite, nickeline, or kupfer-nickel, NiAs, found in the Saxon mines, in Styria, at Leadhills, and in Connecticut; nickel glance, NiAsS; breithauptite, NiSb; millerite or nickel blende, NiS; linnaeite, $(CO,Ni,Fe)_3S_4$; pentlandite, (Ni,Fe)S; nickel ochre or annabergite, $Ni_3(AsO_4)_2,8H_2O$; rewdanskite, $(Ni,Fe,Mg)_3Si_2O_7,2H_2O$, etc. Nickel also occurs frequently in magnetic pyrites, the deposits at Sudbury, Canada, at present supplying about 60 per cent. of the world's production. It consists of pyrrhotine associated with small quantities of copper pyrites, pentlandite, and occasionally millerite. An important source of nickel has been opened out in New Caledonia, where large quantities of a silicate of nickel called garnierite, $2(Ni,Mg)_5Si_4O_{13},3H_2O$, occur.

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[1] *Zeit. anorg. Chem.*, 1906, **51**, 171.

[2] See Link, *Phil. Trans.*, 1726, **34**, 192.

Nickel is an essential constituent of meteoric iron (p. 1211), its presence in extra-terrestrial matter having been first detected by Proust. It is contained also in the sun's atmosphere.

METALLURGY OF NICKEL.

595 The method adopted for the extraction of metallic nickel varies according to the nature of the ore to be treated. Formerly nickel was largely obtained as a by-product from the treatment of complex ores of copper, etc., by long and complicated wet and dry processes, but at the present time most of the nickel is obtained from garnierite and nickeliferous pyrrhotite and chalcopyrite.[1]

The method of treating garnierite, as at present practised, consists in smelting the ore with the addition of calcium sulphate or even alkali waste (chiefly calcium sulphide), for the production of a matte of nickel and iron, together with a slag, consisting of silicates of lime, magnesia, and other bases. This matte, which generally contains about 50 per cent. of nickel, 30 per cent. of iron, and 20 per cent. of sulphur, is either blown in small Bessemer converters similar to those used for enriching copper mattes (p. 425), or is smelted in reverberatory furnaces together with a siliceous flux, yielding in both cases a rich pure nickel sulphide, containing 80 per cent. of nickel and a siliceous iron slag containing a small amount of nickel.

It is, however, impossible to blow this nickel sulphide to the metal, as can be done with copper sulphide, on account of reactions which yield NiO taking place more easily and at a lower temperature than those yielding metallic nickel. The nickel sulphide has therefore to be carefully roasted, generally twice, sometimes with the addition of sodium nitrate, and the nickel oxide washed and dried. The oxide is then pressed into the form of small cubes, and these are strongly ignited with charcoal powder. The reduction takes place from the outside, the metal absorbing carbon and retaining the form of the cubes. The operation is usually carried on in clay crucibles standing on the hearth of a reverberatory furnace, or in a special furnace[1] in which the reduction may be carried on continuously. This consists of a furnace through which vertical fire-clay tubes pass; these tubes are charged at the top with the mixture of crude oxide and coal, and the metal is withdrawn from time to time at the bottom. Commercial nickel contains carbon, as well as small quantities of cobalt, copper, iron, and sulphur.

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[1] Steinhart, *Trans. Inst. Min. and Met.*, 1905-6, **15**, 230. See also *Report of the Royal Ontario Nickel Commission*, 1917.

For sulphides such as the Canadian ores, containing 3 per cent. of nickel, and about 2 per cent. of copper, the process is carried out as follows: the ore is first heap-roasted to oxidise the iron and remove the excess of sulphur. The roasted ore is then smelted in a blast furnace, producing a matte containing 36 to 40 per cent. nickel-copper. This matte is then concentrated, either by being again put through the cupola with a siliceous flux, or by being blown in a converter, to an 80 per cent. nickel-copper matte.

The separation of the nickel from the copper may be effected by what is known as "tops and bottom" smelting, by means of an alkaline sulphide. The matte is mixed with coke and sodium sulphate (salt-cake), 30 tons of salt-cake and 7 tons of coke being used for 50 tons of matte, and is charged into a magnesia-lined open-hearth reverberatory furnace. The mixture is melted down and allowed to stand for five hours in the furnace, being frequently poled. Practically complete solution of the copper sulphide, and any iron sulphide present, is thus effected in the sodium sulphide formed from the salt-cake. The molten charge is then tapped from the furnace and allowed to separate in moulds, or the two strata are tapped separately from the furnace. The nickel sulphide thus obtained may be roasted and reduced as already described. A small amount of nickel is also extracted by a wet method as described under cobalt.

Another method for the treatment of the rich matte consists in granulating it, followed by roasting and leaching out the copper. The leached material is then smelted with suitable fluxes in an electric furnace. The nickel-copper alloy obtained is cast into anodes and refined electrolytically by the Hybinette process, the slimes being treated for platinum, palladium, gold, iridium, etc.

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[1] *Ber. Entw. Chem. Ind.*, 7, 866.

The Mond Process which depends on the formation and decomposition of the volatile nickel carbonyl $Ni(CO)_4$ is very important and interesting.[1]

The ore is mined in the Sudbury region of Ontario and is there roasted, smelted, and bessemerized, as described above, yielding a matte containing 40% Ni, 40% Cu, and less than 1% Fe, the remainder being almost entirely sulphur. This matte is shipped to the refining-works at Clydach, Swansea. It is crushed and calcined at the lowest possible temperature in a current of air. The calcined matte is treated with about 15% sulphuric acid at 80° whereby about 70% of the copper and only about 7% of the nickel together with some of the iron are extracted as sulphates. The copper-extracted matte is filtered off and dried. It is reduced in a stream of water-gas by passing down over a series of shelves in a tower heated to about 330°. The reduced matte is passed by air-tight conveyers to volatilizers which are exactly similar to the reducers, and is thus brought into intimate contact with a stream of water-gas at a temperature not exceeding 50°. Under these conditions the finely-divided nickel combines with the carbon monoxide of the water-gas to yield the carbonyl which is swept over in the stream of gas to the decomposers. These are specially constructed towers filled with nickel shot and heated on the outside by producer-gas to about 180°. The carbonyl is decomposed

$$Ni(CO)_4 = Ni + 4CO.$$

and the carbon monoxide passes on for further extraction. The nickel is deposited on the shot which are prevented from coalescing by being kept in constant motion and so grow individually. An exceptionally pure metal containing nearly 99·9% Ni is thus produced.

The liquors from the copper extraction are crystallized and yield a very pure copper sulphate. The mother-liquor is then re-charged with acid and used for further extraction and crystallization, and this is repeated until it becomes too rich in nickel sulphate. It is then treated with reduced matte when the finely-divided nickel replaces the copper of the remaining copper sulphate yielding a solution of nickel sulphate free from copper. The iron is removed by oxidation and precipitation as ferric hydroxide and the nickel sulphate is crystallized.

In each operation about 70% of the copper and 70% of the nickel are removed, and, after being concentrated by passing through the cycle several times, the residual matte is sufficiently rich in the precious metals to be worked up for them.

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[1] See Mond, *J. Soc. Chem. Ind.*, 1895, **14**. 945.

Pure nickel can be prepared, according to Winkler,[1] by electrolysing a solution of the pure sulphate containing ammonium sulphate and ammonia, a cathode of highly polished nickel being used, and the current passed until the nickel separates from the electrode in thin plates. It is then heated in a current of pure dry hydrogen.

In practice, small quantities of magnesium are often added to molten nickel; this is found to make the metal very fluid before casting, and also renders it malleable, and free from blow-holes due to gas.

596 *Properties.*—Nickel is a lustrous, silver-white metal with a steel-grey tinge. It is very hard and takes a high polish, and may easily be rolled out into thin plates and drawn into wire. The pure metal melts at 1452°, but may be welded below its melting point, and distils in the electric furnace more readily than cobalt.[2] As in the case of iron, when the metal contains carbon it is less malleable and more readily fusible. It has a sp. gr. of 8·35 when cast to 8·9 when rolled, and its average specific heat between 15° and 100° is 0·10842.[3]

Nickel oxidises only with difficulty, even on heating in the air. It decomposes steam very slowly at a red heat with formation of the monoxide, which is also formed when the metal is heated at 200° in nitric oxide.[4] It is slowly soluble in hydrochloric or dilute sulphuric acid, and does not dissolve quickly even in the concentrated acid. On the other hand, it dissolves readily in dilute nitric acid; but if it be dipped into the concentrated acid it becomes "passive," as does iron.

Nickel exists in two allotropic modifications, the transition temperature being between 340° and 360°. The metal is attracted by a magnet below this temperature, but is non-magnetic above it.[5] The transition is also indicated by a sudden change at this temperature in the coefficient of expansion,[6] the electromotive force against copper,[1] the electrical resistance[1] and the rate of cooling.[2]

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[1] *Zeit. anorg. Chem.*, 1894, **8**, 1; see Kohlschütter and Schödl, *Helv. Chim. Acta*, 1922, **5**, 490, 593.

[2] Moissan, *Compt. rend.*, 1906, **142**, 425.

[3] For detailed list of the physical properties of pure and commercial nickel, see Merica, *Chem. Met. Eng.*, 1921, **24**, 73.

[4] Sabatier and Senderens, *Compt. rend.*, 1892, **114**, 1429.

[5] Werner, *Zeit. anorg. Chem.*, 1913, **83**, 275; Honda and Ogura, *Sci. Reports Tôhoku Imp. Univ.*, 1914, **3**, 113.

[6] Harrison, *Phil. Mag.*, 1904, **7**, [6], 626; Jänecke, *Zeit. angew. Chem.*, 1918, **31**, i., 229; *Zeit. Elektrochem*, 1919, **25**, 9.

Nickel, like iron and cobalt, is capable of absorbing hydrogen. The solubility is independent of the superficial area of the metal, so that the phenomenon is one of true solution and not of adsorption. At constant temperature, the solubility in the solid and molten metal is proportional to the square root of the pressure. The gas is more soluble in the molten metal, and when this solidifies about twelve volumes of hydrogen are liberated with much "spitting."[3]

Nickel is now largely employed for coinage, for electro-plating, for the manufacture of many important alloys, and as a catalyst. The pure metal is also used for the manufacture of cooking utensils, and for the manufacture of crucibles which can be used in many laboratory operations, instead of those made of the more costly platinum.

Nickel Coinage.—The application of copper-nickel alloys to the manufacture of small coin was first introduced into Switzerland in 1850. The Swiss pieces of twenty, ten, and five centimes contained respectively fifteen, ten, and five per cent. of silver alloyed with 10 parts of nickel and 12·4 of zinc, the residue being made up of copper. A yellow alloy containing twelve of nickel to eighty-eight of copper was adopted in 1856 by the United States Government for the one cent pieces. In 1860 the Belgian Government instituted a nickel-copper coinage, containing twenty-five of the former to seventy-five of the latter metal, this same alloy being adopted in 1866 by the United States for the five and ten cent pieces, by Brazil in 1872, and by the German Government in 1873 for the five- and ten-pfennig pieces. The application of this alloy rapidly extended to other countries, including many parts of the British Empire, and at the end of 1912 no fewer than forty-nine countries had adopted it, more than four thousand million such coins being then in circulation.

The alloy is very hard, so that the coins are resistant to wear and tear. It is white and of pleasing appearance and does not readily tarnish. Unlike the pure metal, it is not magnetic, and coins made of the alloy may be distinguished from those of pure nickel by this simple test.

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[1] Werner, *loc. cit.*

[2] Baikon, *Int. Zeit. Metallog.*, 1914, **6**, 115; Laschtschenko, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 311.

[3] Sieverts, *Zeit. physikal. Chem.*, 1911, **77**, 591.

It is a very remarkable fact that a coin of the Bactrian King Euthydemos, who reigned about 235 B.C., analysed by Flight,[1] possesses a very similar composition to the alloy in question, viz.: 77·58 per cent. of copper and 20·04 per cent. of nickel.

In 1881, the Swiss Government introduced a new issue of 20 centime pieces made of pure nickel. These coins have proved so successful that many other nations have introduced pure nickel coinage to replace silver, bronze, and even cupro-nickel. At the end of 1912, Switzerland, Austria, Italy, France, Serbia, Montenegro, Mexico, Turkey, and Siam had adopted the metal for small coinage, and about a thousand million pieces were in circulation.[2]

The advantages of a nickel coinage, and especially of pure nickel, are many. First, the metal is more valuable than copper, and consequently, for the same value, the coins can be of smaller size. Secondly, it is extremely tough, and the coins wear so well that replacement costs are extremely small. There is practically no deterioration in the Swiss coins which have been in circulation for forty years. Thirdly, owing to its hardness, nickel is very difficult to work, extensive plant and machinery and highly skilled labour being required for the production of coins, so that the manufacture of counterfeits would not be an attractive and profitable business. Lastly, nickel provides a clean and beautiful coinage. It has a brilliant surface, takes the impress of the die most distinctly and permits, therefore, of the most elaborate designs, a further difficulty thus being placed in the way of the counterfeiter.

In those countries where the silver and nickel coins are of about the same size, the latter are made readily distinguishable by being perforated, as in France, and Belgium, by having scolloped edges, as in India, or by being made square with rounded corners, as in Holland and Ceylon.

Electro-nickel Plating.—Pure nickel is used as the positive pole in processes for the electro-deposition of nickel, which are especially valuable for coating iron and steel with a thin film of pure nickel. If the coating be well deposited, the metal scarcely undergoes any oxidation, but it is found to adhere better when a layer of copper is first deposited on the iron. The process of nickel-plating was first applied to fire-arms in order to preserve them from rusting. Now, however, it is also used for covering various parts of machines, locks, keys, surgical instruments, and other fine iron- and steel-work. A great variety of proposals have been made for the preparation of the liquid used in this process, but the only bath which is practically useful is a solution of pure nickel ammonium sulphate, saturated at a temperature of 20–25°.[1] The salt is only moderately soluble, and consequently, in order to increase the conductivity of the bath, it is usual to add ammonium sulphate or nickel sulphate or sodium chloride. In a neutral solution, there is always a possibility of basic salts being formed and deposited on the cathode, thus spoiling the coating. Boric acid is therefore sometimes also added to the bath.

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[1] The *Numismatic Chronicle*, 8, 395; and *Pogg. Ann.*, 1870, **139**, 507.

[2] See *Report of the Royal Ontario Nickel Commission*, 1917.

The article to be plated is made the cathode, and the anode is of pure nickel either cast or rolled. The cast metal dissolves much more readily than the rolled, but the latter has a more uniform composition and therefore dissolves more evenly and with less waste. In either case, the plating must be done slowly owing to the difficulty with which nickel is soluble, and for the same reason the anode surface is made greater than that of the cathode.

The deposit is usually very thin, and such only is necessary, but attempts to deposit thick layers of nickel have often met with failure. The deposition of thick layers is possible only in solutions absolutely free of iron.[2] Iron is deposited more easily than nickel, and the first layers are therefore richer in it than succeeding ones, so that strains are set up and the deposit flakes off. Working in the hot (above 50°) has been recommended for the production of thick deposits, but these may be obtained quite satisfactorily in the cold in the complete absence of iron.

Nickel plating can be recognised without damaging the plate by placing on it a spot of acid, absorbing this almost immediately with filter-paper, and testing the wet spot on the paper by adding a drop of ammonia to neutralise the acid, then a drop of acetic acid and a drop of dimethyl glyoxime solution, when a red coloration is produced.[3]

The thickness of the plating can also be determined without damaging the plate.[4] The article is first thoroughly cleaned; a few drops of a solution containing by volume 1 part of nitric acid, 2 parts of hydrogen peroxide, 3 parts of hydrochloric acid, and 5 parts of water are placed on it; after two minutes a drop of ammonia is added; the liquid is then removed and its colour examined. If the plating is on copper, a blue colour indicates a nickel deposit of less than 1 mgr. per sq. cm., and if on iron a brown colour indicates a deposit of less than 4 mgr., per sq. cm. Other thicknesses can be estimated by varying the time of contact of the solution with the metal.

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[1] *Ber. Entw. Chem. Ind.*, i., 874; Bennett, Kenny, and Dugliss, *J. Physical Chem.*, 1914, **18**, 373.

[2] See Engemann, *Zeit. Elektrochem.*, 1911, **17**, 910.

[3] Bianchi and di Nola, *Boll. Chim. farm.*, 1910, **49**, 517.

[4] Pontio, *Compt. rend.*, 1915, **161**, 175.

Nickel can also be successfully plated on aluminium if this metal be first either subjected to a sand-blast[1] or else scoured with milk of lime and then dipped in an acid bath of a metallic chloride such as ferric chloride.[2]

ALLOYS OF NICKEL.

597 In 1825, Thénard in his *Traité de Chimie* remarked that nickel was not employed for any practical purpose, although Engeström had pointed out so long ago as 1776 that Chinese packfong is an alloy of copper, zinc, and nickel. Packfong, or rather Pack-Tong, means white copper, and Tong-Pack probably means the same thing, although in Europe this name, changed to tomback, is employed to describe a particular kind of brass. Since the middle of the eighteenth century a white alloy had been prepared at Suhl, in Hanneberg, from old copper slag; and Brandes in 1823 showed that this white copper consisted chiefly of an alloy of copper and nickel, and thus commenced the manufacture of nickel alloys known under the name of German silver, nickel silver, or argentan, a trade which has now attained large dimensions.

Nickel Silver, or *German Silver*, is an alloy of copper, nickel, and zinc, containing its constituents in varying proportions according to the method of preparation and the articles for which it is used. As a rule, five parts of copper, two of nickel, and two of zinc are used, thus giving rise to an alloy which has the appearance of silver alloyed with one-quarter of copper. In Sheffield, eight parts of copper, 3·5 of zinc, and three of nickel are employed. A commoner and yellowish alloy is obtained when less nickel is used, whereas if more nickel be employed the alloy has a bright white colour, and takes a high, silvery polish. The addition of 2·5 per cent. of iron makes the alloy whiter, but also harder and more brittle.

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[1] Guillet and Gasnier, *Compt. rend.*, 1920, **170**, 1253.

[2] Mazuir, *Ann. Chim. anal.*, 1920, [2], **2**, 335.

The following table gives the composition of several of these alloys: No. I. is Chinese packfong analysed by Fyfe; II. the same, by Kefferstein; III. German silver by Bolley; IV.–VI. various samples of nickel silver used in Birmingham for articles to be plated, and analysed by Louyet; VII. an alloy from Sheffield distinguished by extraordinary elasticity and used for the friskets of printing presses, analysed by Elsner; and VIII. an alloy used for strong castings, such as high pressure steam fittings.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Copper .	40·4	26·3	54·0	63·34	62·40	62·63	57·4	70·0
Zinc . .	25·4	36·8	28·0	17·01	22·15	26·05	25·0	10·0
Nickel .	31·6	36·8	18·0	19·13	15·05	10·85	13·0	20·0
Iron . .	2·6	—	—	trace	trace	trace	3·0	—
	100·0	99·9	100·0	99·48	99·60	99·53	98·4	100·0

In preparing nickel silver it is usual to melt the zinc with half the weight of copper which it is ultimately to contain, this alloy being then cast into thin plates. The other half of the copper is then fused with the nickel under a layer of charcoal powder, and the copper-zinc alloy is added. After cooling, the alloy possesses a crystalline structure, and this is got rid of by hammering and rolling, again heating, and allowing to cool. When it has once lost its crystalline structure, it can be worked like brass, and although it is harder and tougher it may be rolled out to foil and drawn to wire. Hence this alloy is used for a great number of purposes, as it is much cheaper than silver, and less apt to be discoloured. On the other hand, it is more readily attacked by liquids, and for this reason nickel silver articles employed for household use are generally covered with a coating of silver. The addition of small quantities of aluminium has been shown to improve greatly the quality and appearance of nickel silver.[1]

Nickel and copper alone mix in all proportions, giving many important alloys. These alloys of nickel, on fusing, absorb a considerable quantity of gas, and the higher the temperature and the percentage of nickel the greater is the quantity absorbed. Künzel found that if an alloy of eighty parts of copper and twenty of nickel be fused in a crucible half filled with the mixture, and this quickly cooled, the mass froths up from the evolution of gas, and runs over the top of the crucible. If a copper-nickel alloy be granulated in water, yellow globules are obtained, and these are frequently so thin that they float on the surface of the water.[1]

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[1] See Guillet, *Compt. rend.*, 1914, **158**, 704.

An alloy of 75 per cent. copper and 25 per cent. nickel is utilised in many countries for the manufacture of currency.

An alloy of nickel with four parts of copper, known as *cupro-nickel,* is used for the casing of bullets to be employed with small-bore rifles. A very similar alloy containing 14 to 16 per cent. of nickel and 84 to 86 per cent. of copper is known as *Benedict metal.*

Monel metal is an alloy of nickel and copper possessing remarkable mechanical properties. It is made directly from the nickel-copper matte produced from the Sudbury ores (see p. 1358), and is therefore a "natural" alloy. It contains from 60 to 72 per cent. of nickel, from 0·5 to 6·5 per cent. of iron and manganese, the remainder being copper.

The addition of nickel to copper greatly increases its electrical resistance, the maximum resistance being obtained with about 40 per cent. of nickel; the resulting alloy is known as *Constantan,* on account of its low temperature coefficient.

Other high resistance alloys containing nickel are *Platinoid,* consisting of 60 per cent. of copper, 24 per cent. of zinc, 14 per cent. of nickel, and 1 to 2 per cent. of tungsten; *Rheostan,* containing 52 per cent. of copper, 18 per cent. of zinc, 25 per cent. of nickel, and 5 per cent. of iron; *Manganin,* containing 4 to 40 per cent. of nickel, 60 to 80 per cent. of copper, with 1 to 12 per cent. of manganese; *Nichrome,* containing 60 per cent. of nickel, 14 per cent. of chromium, and 15 per cent. of iron; and *Illium,* containing about 60 per cent. of nickel, 6 per cent. of copper, 21 per cent. of chromium, 4 per cent. of molybdenum, 2 per cent. of tungsten, and 1 per cent. each of iron, aluminium, manganese, and silicon.[2] The two last named are also remarkably resistant to corrosion and to the action of acids, and possess great mechanical strength.

By far the most important application of nickel for alloys, however, is in the manufacture of *nickel-steel,* and fully half the world's production of nickel is used for this purpose. Nickel-steel contains usually 2·5 to 3·5 per cent. of nickel, which gives it a far greater tensile strength and ductility and also renders it more resistant to wear and to corrosion. Apart from its use for armaments, nickel-steel is largely used in engineering, notably for bridge-building and for crank-shafts and other important parts of machinery. Nickel-steel is the term applied to alloys of iron containing less than 5 per cent. of nickel, but other alloys containing a higher percentage of nickel are also of importance. *Invar* contains 35 per cent. of nickel and about 0·5 per cent. of carbon. Its coefficient of expansion is practically nil, and as it takes a high polish and is not corrodible, it is largely used in the manufacture of chronometers. *Platinite* containing 46 per cent. of nickel and 0·15 per cent. of carbon has practically the same coefficient of expansion as platinum and is therefore used for fusing into glass instead of that expensive metal.

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[1] *Ber. Entw. Chem. Ind.,* i., 867.

[2] Parr, *Journ. Amer. Chem. Soc.,* 1915, **37,** 2515; *J. Soc. Chem. Ind.,* 1915, **34,** 1097.

Nickel as a Catalyst.—Nickel in the finely divided state is a very important catalyst. It is readily made by reducing the oxide in hydrogen, but its activity depends upon the mode of preparation. The reduction should be carried out at as low a temperature as possible, and for this reason the oxide employed should be obtained by precipitation or by ignition at the lowest possible temperature. A very active material is made by reducing the hydroxide in hydrogen at a temperature not exceeding 300°. The metal obtained in this way is pyrophoric, and as the oxide produced on allowing this to oxidise is more readily reducible than the original, a still more active catalyst can be obtained by allowing it to oxidise and then reducing it again.[1] The preparation of the active metal is best made in the vessel in which the catalysed reaction is to be carried out so that no oxidation may occur through any transference.

The metal is very readily "poisoned" by certain substances, notably the halogens, sulphur, phosphorus, and arsenic. The oxide is therefore prepared from the nitrate rather than the sulphate or chloride, but if the latter are used the precipitated hydroxide must be most carefully washed. The hydrogen used for reduction and for subsequent reactions must be thoroughly freed from these substances, and this is best done by passing the gas first over copper turnings heated to redness and then through caustic potash. Even though all the substances are highly purified, the activity of the nickel gradually becomes enfeebled during use owing to traces of toxic substances which gradually accumulate, and also to non-volatile matter condensing on the surface of the metal and thus preventing contact with the reacting substances.[1]

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[1] Senderens and Aboulenc, *Bull. Soc. chim.*, 1912, [4], 11, 641.

The reactions are carried out simply by passing the vapour of the substance, or the vapour mixed with hydrogen, through a layer of the finely divided metal maintained at the requisite temperature. In order to afford a larger active surface to the action of the vapours, the metal is sometimes deposited on a "carrier" such as pumice-stone or fire-clay.

When acetylene is passed through finely divided nickel, even in the cold, it is completely decomposed, part of it being converted into benzene and other polymerides, but the greater part being split up into carbon and hydrogen.[2] Ethylene is completely decomposed by the metal at about 300°, chiefly into methane, with traces of higher hydrocarbons, and partly into hydrogen, carbon being deposited,[3] $C_2H_4 = CH_4 + C$.

The catalytic activity of nickel has been the subject of much research, chiefly by Sabatier and Senderens and their co-workers,[4] especially in reductions, which are easily effected by passing the vapour of the substance with excess of hydrogen over the catalyst. Thus, by the simple addition of hydrogen, the unsaturated hydrocarbons, including those of the benzene series, are converted into the corresponding saturated compounds, and aldehydes and ketones yield the corresponding alcohols.[5] Carbon monoxide and dioxide are reduced to methane and nitro-compounds to amines. In general, these reactions proceed at a low temperature, and their rate increases with rise of temperature up to about 180°, where they proceed very rapidly. At higher temperatures, the reaction is often reversed, hydrogen being liberated, and at about 350° the higher organic compounds are decomposed chiefly into simple hydrocarbons with deposition of carbon.[6]

This fact finds an important technical application of finely divided nickel as a catalyst for the removal of carbon disulphide from coal-gas, thus reducing its sulphur content considerably.

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[1] Sabatier, *J. Soc. Chem. Ind.*, 1914, **33**, 733; Crossley, *ibid.*, 1914, **33**, 1135.

[2] Moissan and Moureu, *Compt. rend.*, 1896, **122**, 1240.

[3] Sabatier and Senderens, *ibid.*, 1897, **124**, 616.

[4] *Ibid.*, *Ann. Chim. Phys.*, 1905, **4**, 319; *ibid.*, 1909, **16**, 70; Sabatier, *Ber.* 1911, **44**, 1984.

[5] See also Brochet, *Compt. rend.*, 1914, **158**, 1351; Brochet and Bauer, *ibid.*, 1914, **159**, 190; Brochet and Cabaret, *ibid.*, 1914, **159**, 326; Sandonnini, *Gazz.*, 1922, **52**, [i], 394.

[6] Sabatier and Gaudion, *Compt. rend.*, 1919, **168**, 670; Mailhe, *Chem. Zentr.*, 1921, [1], 717.

The catalyst is made by impregnating balls of fire-clay with a nickel salt. They are filled into towers and the salt is reduced to metal in a stream of coal-gas. The towers are kept at a temperature of about 400°, and the gas to be purified is passed through. The carbon disulphide is decomposed, the carbon being deposited and the sulphur uniting with the hydrogen of the gas to form hydrogen sulphide, which is then absorbed by ferric oxide in the usual manner (Vol. I, p. 882). After running for some weeks a tower becomes so filled with carbon that it ceases to work. It is then blown out with inert gas (carbon dioxide), and a current of air is passed through. This completely burns the carbon, which is swept away as carbon dioxide, and converts the nickel to oxide. The tower is then again swept out with carbon dioxide to displace the air, and put into operation again. The coal-gas first reduces the oxide to nickel and this is as active as before in the removal of the carbon disulphide.

The oxides of nitrogen when passed with hydrogen over finely divided nickel are reduced to nitrogen and ammonia, the relative quantities depending on the composition of the mixture, the rate at which it is circulated over the nickel, the temperature of the reaction, and also the state of the catalyst.[1] Sulphur dioxide and hydrogen, when similarly treated, yield hydrogen sulphide,[2] while if hydrogen be passed over a mixture of finely divided nickel and phosphoric oxide, phosphine is obtained.[3]

By far the most important application of the catalytic property of nickel is in the hydrogenation or "hardening" of oils for the manufacture of soap and of margarine. Very few details have been published of the methods in use, but the process consists in treating the liquid oil with purified hydrogen in the presence of nickel.[3] The catalyst is prepared by reducing the oxide as already described, and is introduced into the oil without exposure to air, or, more usually, the oxide itself is added to the oil and reduced *in situ* by the hydrogen. The formate or oxalate may be used instead of the oxide, and are said to give a very active metal.[4] A new method has been suggested in which nickel oxide is treated in a tube with a mixture of carbon monoxide and hydrogen, and the nickel carbonyl thus formed is swept over into the hot oil and there instantly decomposed, yielding the metal in a very finely divided and active condition.[1] The mixture of oil and catalyst is kept at a temperature depending on the constitution of the oil and the amount of nickel added, but generally about 150° to 250°, and purified hydrogen is bubbled through with constant stirring. In some cases treatment with hydrogen under pressure has been found to be more rapid and satisfactory, and it is claimed that the nickel is then not so sensitive to impurities in the oil and hydrogen.[2] After hydrogenation, the oil is filtered in order to remove the nickel, and the metal thus recovered is available for further use.

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[1] Guye and Schneider, *Helvetica Chim. Acta*, 1918, 1, 33.

[2] Neogi and Adhicäry, *Zeit. anorg. Chem.*, 1910, 69, 209.

[3] See Ellis, *J. Soc. Chem. Ind.*, 1912, 31, 1155; Armstrong and Hilditch, *Proc. Roy. Soc.*, 1921, [*A*], 100, 240.

[4] Brochet, *Bull. Soc. chim.*, 1920, [4], 27, 897, 899.

The original oil is an unsaturated compound, and is thus converted into a saturated body of higher melting point. For example, oleic acid, m.p. 14°, is readily transformed into stearic acid, m.p. 69°, and whale oil (which is worked up in very large quantities) yields a solid of m.p. about 54°.

Some believe that nickel oxide acts as a catalyst,[3] and that when the oxide is added to an oil and hydrogen passed through, it is reduced to a sub-oxide which forms a black, colloidal solution with the oil and is responsible for the catalysis.[4] Most authorities, however, hold that all active oxides contain the finely divided metal which alone can act as a catalyst.[5]

Colloidal Nickel.—Nickel can be obtained in colloidal aqueous solution by coating iron or zinc wires with the metal and then "pulverising" it by Bredig's electrical method.[6] It has also been obtained as a colloid in organic solutions by a spark discharge from the granulated metal under the liquid.[7]

If nickel be heated in the Bunsen flame and plunged into cold water, a solution is obtained containing the metal and also the hydroxide in colloidal solution.[8]

A colloidal solution of pure nickel is obtained by heating a solution of nickel carbonyl in benzene.[9] This yields a beautiful violet-grey solution, whereas all the other methods of preparation give a brown product.

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[1] Lessing, *J. Soc. Chem. Ind.*, 1913, **32**, 917.

[2] Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 302.

[3] Bedford and Erdmann, *J. pr. Chem.*, 1913, [2], **87**, 425; Senderens and Aboulenc, *Bull. Soc. chim.*, 1915, [4], **17**, 14.

[4] Bedford and Erdmann, *loc. cit.*, Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, **54**, [*B*], 113.

[5] Meigen and Bartels, *J. pr. Chem.*, 1914, [2], **89**, 290; Normann and Pungs, *Chem. Zeit.*, 1915, **39**, 29, 41; Normann, *Chem. Zeit.*, 1916, **40**, 757; Armstrong and Hilditch, *Proc. Roy. Soc.*, 1921, [*A*], **99**, 490; Kelber, *Ber.*, 1921, **54**, [*B*], 1701; Normann, *ibid.*, 1922, **55**, [*B*], 2193.

[6] Billitzer, *Ber.*, 1902, **35**, 1929.

[7] Svedberg, *Ibid.*, 1905, **38**, 3616; *ibid.*, 1906, **39**, 1705.

[8] Kimura, *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, 1913, **5**, 211.

[9] Ostwald, *Kolloid Zeit.*, 1914, **15**, 204.

Reduction of colloidal nickelous hydroxide or of the freshly precipitated hydroxide in the presence of sodium protalbinate as protective colloid, by means of hydrogen with colloidal palladium as catalyst, also yields a colloidal solution of nickel.[1]

A colloidal solution is similarly produced by reducing nickel formate, acetate, or freshly precipitated hydroxide, dissolved or suspended in glycerine, with hydrogen at 200° to 210° or with hydroxylamine, hydrazine hydrate, formaldehyde, or hypophosphorous acid. Gelatin or gum arabic is used as a protective colloid. Addition of water precipitates a brown mass containing about 30 per cent. of nickel, and this is soluble again in alcohol or glycerine.[2]

COMPOUNDS OF NICKEL.

Nickel and Oxygen.

598 A large number of different oxides of nickel have been described, the most important being the monoxide, NiO, which is the only one yielding a corresponding series of salts. In addition, the sesquioxide, Ni_2O_3, has been prepared, and peroxides are obtained by the electrolytic oxidation of the metal. Trinickel tetroxide,[3] Ni_3O_4, has been described together with several other oxides such as Ni_4O_7,[4] Ni_6O_7,[5] and Ni_3O_5,[6] as well as the suboxides Ni_2O,[7] Ni_3O,[8] and Ni_4O,[9] but these are probably mixtures of the monoxide with peroxide in the one case and nickel in the other.[10]

Nickel Monoxide or Nickelous Oxide, NiO.—This substance occurs as bunsenite at Johanngeorgenstadt in Saxony, in vitreous, translucent, pistachio-green, regular octahedra having a specific gravity of 6·398. It may be obtained by strongly heating the hydroxide, sesquioxide, carbonate, or nitrate in the form of a green, crystalline powder, which becomes deep-yellow on heating. If nickel borate be ignited with lime in a pottery furnace and the mass treated with hydrochloric acid, nickel oxide remains behind in green cubo-octahedra which have a specific gravity of 6·8 (Ebelmen), whilst if the metal be ignited in a current of steam, pale olive-green crystals of the oxide are formed. When heated in the air, nickelous oxide at first absorbs oxygen, but loses it again at a higher temperature. In the electric furnace, it melts and solidifies in green crystals,[1] which may also be obtained as minute cubo-octahedra of specific gravity 7·45 by heating with excess of potassium chloride at 1000°.[2] It is readily reduced by hydrogen at 220°,[3] by carbon monoxide at 120°, and by solid carbon at 450°, but these temperatures depend on the physical condition of the oxide. The dissociation pressures of nickelous oxide have been measured between 800° and 1245°.[4]

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[1] Paal, *Ber.*, 1914, **47**, 2202.

[2] Kelber, *Ibid.*, 1917, **50**, 1509.

[3] Baubigny, *Compt. rend.*, 1878, **87**, 1082; Dudley, *J. Amer. Chem. Soc.*, 1896, **18**, 901; Bellucci and Rubegni, *Atti R. Accad. Lincei*, [5], 1906, **15**, ii., 778.

[4] Wicke, *Jahresb.*, 1865, 267.

[5] Schröder, *Journ. Chem. Soc.*, 1890, **58**, 1213.

[6] *Chem. News*, 1879, **39**, 81.

[7] Müller, *Pogg. Ann.*, 1869, **136**, 59; Tschugaev and Choplin, *Compt. rend.*, 1914, **159**, 62.

[8] Moore, *Chem. News*, 1895, **71**, 81.

[9] Sabatier and Espil, *Compt. rend.*, 1914, **158**, 668.

[10] See Wöhler and Balz, *Zeit. Elektrochem.*, 1921, **27**, 406.

Nickelous oxide, like cobaltous oxide, forms compounds when fused with many other metallic oxides. With alumina, a well defined blue aluminate, NiO,Al_2O_3, is produced, with stannic oxide a green stannate, and with zinc oxide a green zincate. These compounds dissolve in excess of the oxide to form solid solutions the colour of which varies with the relative proportions of the constituents. With magnesium oxide, nickelous oxide forms mixed crystals which are intermediate in colour between the two components, and with manganous oxide mixed crystals of a yellowish-green colour.[5]

Nickel Hydroxide, $Ni(OH)_2$, is thrown down when a solution of a nickel salt is heated with potash or soda, as an apple-green precipitate slightly soluble in water. It dissolves in ammonia with a blue colour, and separates out as a green, crystalline powder on boiling the ammoniacal solution. Nickel hydroxide has been prepared in colloidal solution by using sodium lysalbate as a protective colloid.[6] It may also be obtained by precipitating nickel chloride with potassium hydroxide and washing free from electrolytes or by dialysing nickel tartrate solution.[7]

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[1] Moissan, *Ann. Chim. Phys.*, 1880, [5], **21**, 199; *Compt. rend.*, 1892, **115**, 1034.

[2] Hedvall, *Zeit. anorg. Chem.*, 1915, **92**, 361.

[3] Ipatieff, *J. pr. Chem.*, 1908, **77**, 513.

[4] Foote and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1344.

[5] Hedvall, *Zeit. anorg. Chem.*, 1918, **103**, 249.

[6] Paal and Brünjes, *Ber.*, 1914, **47**, 2200.

[7] Tower and Cooke *J. Phys. Chem.*, 1922, **116**, 231.

The salts of nickel are derived from the monoxide. In the anhydrous condition, and formed from colourless acids, they are usually yellow-coloured, whilst in the hydrated state they possess an apple-green to an emerald-green colour. The soluble normal salts have a slightly acid reaction and a sweetish, astringent, metallic taste, and act as emetics.

Nickel Sesquioxide, Ni_2O_3, is a black powder obtained by gentle ignition of the nitrate or carbonate in the air, and is converted at a higher temperature into the monoxide. When the sesquioxide is heated in the oxy-coal-gas flame it yields metallic nickel,[1] which on cooling becomes covered with a film of oxide. It dissolves in sulphuric and nitric acids with evolution of oxygen, and in hydrochloric acid with evolution of chlorine; with ammonia, nitrogen is evolved:

$$3Ni_2O_3 + 2NH_3 + 3H_2O = 6Ni(OH)_2 + N_2.$$

When potassium is burnt in the air in nickel vessels, and the product treated with water, black prisms remain having the composition $Ni_2O_3,2HO$, which rapidly oxidise organic substances.[2] It appears most probable that the sesquioxide is a compound of the monoxide and dioxide, NiO,NiO_2, and is to be regarded as nickelous nickelite.

When chlorine is passed through nickelous hydroxide suspended in water, or when a solution of a nickel salt is warmed with an alkali hypochlorite, a black precipitate is formed which is generally regarded as *nickel trihydroxide*, $Ni(OH)_3$, corresponding to the sesquioxide. According to Bellucci and Clavari,[3] however, this substance is in reality the hydrated dioxide, NiO_2,xH_2O, which rapidly loses oxygen.

Nickel Dioxide, NiO_2, has not been prepared in the anhydrous state, but a compound of this oxide and baryta termed *barium nickelite*, $BaO,2NiO_2$, is formed when barium carbonate is strongly heated with nickel sesquioxide in the electric furnace. It forms dark coloured crystals of sp. gr. 4·8, which are rapidly decomposed by hot water and dissolve in hydrochloric acid with evolution of chlorine.[4]

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[1] Road, *Journ. Chem. Soc.*, 1894, **65**, 314.

[2] Hofmann and Hiendlmaier, *Ber.*, 1906, **39**, 3184.

[3] *Gazz.*, 1905, **14**, ii., 234; *Atti R. Accad. Lincei*, 1907, [5], **16**, i., 647; compare Pellini and Meneghini, *Zeit. anorg. Chem.*, 1908, **60**, 178; Tanatar, *Ber.*, 1909, **42**, 1516; Tubandt and Riedel, *ibid.*, 1911, **44**, 2565; *Zeit. anorg. Chem.*, 1911, **72**, 219.

[4] Dufau, *Compt. rend.*, 1896, **123**, 495.

A peroxide of nickel, of uncertain composition, is formed by the electrolytic oxidation of the metal, and plays a part in the Jungner-Edison accumulator.[1] According to Hollard,[2] the *tetroxide*, NiO_4, is produced by the electrolysis at 70° of a very dilute solution of a nickel salt containing chromic acid and an alkali pyrophosphate.

NICKEL AND THE HALOGENS.

599 *Nickel Fluoride*, NiF_2, is obtained by dissolving the hydroxide or carbonate in hydrofluoric acid and evaporating, when blue-green crystals of $NiF_2,3H_2O$ separate.[3] These are decomposed by boiling water with formation of an insoluble pale green oxyfluoride. The acid salt, $NiF_2,5HF,6H_2O$, is also known.[4]

The anhydrous fluoride is obtained by heating the chloride with ammonium fluoride in a current of hydrogen fluoride.[5] It forms volatile, green prisms of specific gravity 4·63, which are not attacked by mineral acids, but are reduced by hydrogen.

Nickel fluoride forms double salts with the alkali fluorides.

Nickel Chloride, $NiCl_2$.—Finely divided nickel burns with a bright light when it is slightly heated in dry chlorine gas, forming yellow scales resembling mosaic gold. If a solution of the oxide or carbonate in hydrochloric acid be evaporated to dryness, the anhydrous chloride is obtained as a yellow, earthy mass which dissolves readily in water with evolution of heat. On gently heating for some time in the air it evolves chlorine, leaving a residue of the oxide. In absence of air, on the other hand, it can be sublimed, and is then obtained in golden scales which, when boiled for some time with caustic potash, are completely converted into the hydroxide. They become gradually coloured green on exposure to the air owing to the absorption of moisture, and are then easily soluble in water. The salt, $NiCl_2,6H_2O$, is obtained in short, six-sided prisms on concentrating the solution; these are easily soluble in water and in alcohol. The hexahydrate is stable in contact with its saturated solution up to about 70°.[6] Mono- and di-hydrates are also known.

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[1] See Zedner, *Zeit. Elektrochem.*, 1905, **11**, 809; 1906, **12**, 463; 1907, **13**, 752; Foerster, *ibid.*, 1907, **13**, 414; 1908, **14**, 17; Riesenfeld, *ibid.*, 1906, **12**, 621.

[2] *Compt. rend.*, 1903, **136**, 229.

[3] Compare Costăchescu, *Ann. Sci. Univ. Jassy*, 1911, **7**, 5.

[4] Edminster and Cooper, *J. Amer. Chem. Soc.*, 1920, **42**, 2419.

[5] Poulenc, *Compt. rend.*, 1892, **114**, 1426.

[6] Étard, *Ann. Chim. Phys.*, 1894, [7], **2**, 539.

The anhydrous chloride absorbs ammonia at the ordinary temperature, swelling up to a white powder possessing a slightly violet tinge, and having the composition $NiCl_2,6NH_3$. The same compound is obtained in blue octahedra by dissolving the chloride in ammonia and allowing the solution to cool. This salt readily evolves ammonia when exposed to the air. It is easily soluble in water, but less so in strong alcohol. A diammoniate and monammoniate have also been prepared.[1] Similar compounds are formed by the bromide and iodide.

Nickel Bromide, $NiBr_2$.—Finely divided nickel absorbs bromine vapour when heated in it, becoming incandescent. In absence of air, the bromide sublimes at a red heat in golden scales. It is also formed by the addition of bromine to finely divided nickel under ether. A yellow compound, $NiBr_2,(C_2H_5)_2O$, is obtained, and this, on heating, loses its ether and yields nickel bromide.[2] The anhydrous salt deliquesces on exposure to air and is readily soluble in water. The solution, which is also obtained by bringing the metal in contact with bromine and water, gives on evaporation deliquescent needles of $NiBr_2,3H_2O$. A dihydrate, hexahydrate, and nonahydrate have also been prepared.

Nickel Iodide, NiI_2.—If nickel powder reduced in hydrogen be heated with iodine, or if the hydroxide be dissolved in hydriodic acid, the solution evaporated to dryness in absence of air, and the solid heated, nickel iodide sublimes in iron-black scales. The solution when evaporated to a syrup deposits bluish-green, very deliquescent prisms having the composition $NiI_2,6H_2O$.

Nickel Chlorate, $Ni(ClO_3)_2$, is obtained by double decomposition of nickel sulphate and barium chlorate solutions, and forms three hydrates containing respectively 6, 4, and 2 molecules of water.[3] The *perchlorate* made by dissolving the hydroxide or carbonate in perchloric acid,[4] gives hydrates with 9, 6, 5, and 4 molecules of water, and also forms a hexammoniate.[5]

Nickel Iodate, $Ni(IO_3)_2$, forms a tetrahydrate and two isomeric dihydrates. The tetrahydrate loses water, iodine, and oxygen below 100°. The dihydrate exists in two isomeric forms. The α-variety is made by the action of nickel nitrate and iodic acid at 25–30°, and is converted into the β-form by warming in the presence of water to 50°. The α-form is only slightly soluble in water and the β-form still less soluble.[1]

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[1] Biltz and Fetkenheuer, *Zeit. anorg. Chem.*, 1913, **83**, 163.

[2] Ducelliez and Raynaud, *Compt. rend.*, 1914, **158**, 2002.

[3] Meusser, *Ber.*, 1902, **35**, 1414.

[4] Goldblum and Terlikowski, *Bull. Soc. chim.*, 1912, [4], **11**, 103, 146.

[5] Salvadori, *Gazz.*, 1912, **42**, [1], 458.

NICKEL AND SULPHUR.

600 *Nickel Subsulphide*, Ni_2S, is obtained as a bronze-yellow, non-crystalline mass when the monosulphide is heated in the electric furnace, and on further heating loses the remainder of the sulphur, forming metallic nickel.[2]

Nickel Monosulphide, NiS, occurs as millerite, being occasionally found in brass-yellow rhombohedra, but more commonly in capillary crystals. When nickel and sulphur are heated together above the melting point of the latter, this same compound is formed with incandescence as a bronze-yellow, brittle mass which is not soluble in hydrochloric or sulphuric acid, but dissolves in nitric acid or aqua regia. It is also obtained by passing hydrogen sulphide over nickel at a red heat. The black, hydrated sulphide is precipitated when ammonium sulphide is added to a nickel salt. This is difficultly soluble in hydrochloric acid, but slightly soluble with a brownish colour in ammonia, as well as in yellow ammonium sulphide and other alkaline polysulphides; it is precipitated from these solutions on exposure to the air, or on addition of acetic acid. In the moist state it oxidises readily on exposure to the air. When a solution of a nickel salt is heated with sodium thiosulphate, the monosulphide is obtained in the form of a dense black precipitate which does not undergo alteration on exposure to the air, and which is not acted upon by boiling hydrochloric acid.

The sulphide is not precipitated by sulphuretted hydrogen in presence of dilute hydrochloric acid, and yet the precipitated sulphide, when obtained from an alkaline solution, is found to be insoluble in dilute hydrochloric acid. It appears probable, therefore, that a rapid change occurs in the freshly precipitated sulphide, and that it thus passes into a form which is insoluble in dilute hydrochloric acid.[3] There are probably three isomeric forms of the sulphide. The α-sulphide is the form chiefly produced when dilute solutions of nickel salts are slowly mixed with dilute solutions of alkali sulphides at the ordinary temperature and in the absence of air. It is readily soluble in the cold in mineral acids of concentration as low as 0·01*N*. It is quite stable in absence of air when kept in contact with pure water, but in contact with solutions in which it is slightly soluble it is transformed into the β- and γ-varieties. The β-sulphide is obtained when a solution of nickel acetate acidified with acetic acid is precipitated with hydrogen sulphide. It is almost insoluble in 2*N*-hydrochloric acid in the cold, but dissolves rapidly on boiling. The γ-sulphide is obtained by boiling the β-form with acetic acid. It is practically insoluble in boiling 2*N*-hydrochloric acid. One form is thus converted into another by treatment with a reagent which has a slight solvent action on it but not on the product. The difference between the three forms is supposed to be due to differences in molecular complexity.[1]

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[1] Mousser, *Ber.*, 1901, **34**, 2432.

[2] Mourlot, *Compt. rend.*, 1897, **124**, 768.

[3] See Thiel and Ohl, *Zeit. anorg. Chem.*, 1909, **61**, 396.

The freezing-point curve for mixtures of nickel and sulphur[2] shows that the only compound capable of existence in contact with the melt is Ni_3S_2, melting at 787°. NiS, Ni_3S_4, and NiS_2 also exist, but dissociate below the melting point.

Linnaeite, $(Ni,Co,Fe)_3S_4$, is an important nickel ore occurring at various places in considerable masses.

Nickel Sesquisulphide, Ni_2S_3.—A black precipitate having approximately this composition is obtained by acting on nickel carbonyl with sulphur dissolved in carbon disulphide.[3]

Nickel Disulphide, NiS_2, is obtained as an impalpable iron-grey powder by strongly heating a mixture of nickel carbonate, potassium carbonate, and sulphur, the residue being lixiviated with water.

Nickel Sulphite, $NiSO_3$, is obtained by dissolving the hydroxide in sulphurous acid. It crystallises with 4 or 6 molecules of water. It dissolves in ammonia to give a hydrated ammoniate, $NiSO_3,3NH_3,3H_2O$, and forms a double salt with ammonium sulphite.

Nickel Sulphate, $NiSO_4$.—This salt was first obtained in the pure and crystalline condition in 1775 by Bergman. In order to prepare it, nickel or its hydroxide or carbonate is dissolved in dilute sulphuric acid. The evaporation of the neutral solution at the ordinary temperature yields green, rhombic prisms of the heptahydrate, $NiSO_4,7H_2O$, isomorphous with magnesium sulphate, and with the corresponding iron and cobalt sulphates. The heptahydrate is known also as nickel vitriol, or morenosite, occurring in acicular crystals, and as a fibrous efflorescence on certain nickel ores. On prolonged exposure to the air, the heptahydrate changes into aggregates of blue tetragonal crystals of the hexahydrate. It has long been thought that this change is brought about by the action of sunlight,[1] but it is really simply a case of efflorescence.[2] If the crystals are in an atmosphere saturated with water vapour, no change takes place even in the strongest light, but, on the other hand, if the atmosphere be dry the change occurs in the dark. This latter compound may be prepared by the slow evaporation at the ordinary temperature of solutions containing 30 per cent. sulphuric acid; it is stable in contact with its saturated solutions between 32° and 53°.[3] If the heptahydrate or the blue hexahydrate is left in contact with the saturated solution above 54°, it is converted into bright green, monoclinic crystals, which have also the composition $NiSO_4,6H_2O$. The hexahydrate is therefore dimorphous. At a temperature about 118° the hexahydrate is transformed into the dihydrate, and if heated above 280°, the salt loses the whole of its water. A tetrahydrate is obtained by crystallising the heptahydrate from sulphuric acid of specific gravity 1·4. One hundred parts of saturated solution contain (Steele and Johnson):

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[1] Thiel and Gessner, *Zeit. anorg. Chem.*, 1914, 86, 1; *Chem. Zentr.*, 1914, I, 18.

[2] Bornemann, *Metallurgie*, 1908, 5, 13; 1901, 7, 667.

[3] Dewar and Jones, *Journ. Chem. Soc.*, 1904, 85, 211.

At	0°	15°	30°	44·7°	50°	60°	80°	90°	
$NiSO_4$	21·4	25·5	29·8	32·4	33·4	35·4	38·7	43·4	parts.

Various basic sulphates have been described.[4]

The anhydrous sulphate absorbs ammonia, becoming strongly heated and increasing in bulk, forming a violet-white powder with the composition $NiSO_4,6NH_3$. On dissolving the sulphate in strong ammonia and cooling, or allowing the solution to evaporate over sulphuric acid, transparent, dark blue, tetragonal prisms crystallise out having the composition $NiSO_4,4NH_3,2H_2O$. A compound of the formula $2NiSO_4,10NH_3,7H_2O$ has also been described.

Nickel Ammonium Sulphate, $(NH_4)_2SO_4,NiSO_4,6H_2O$.—This salt is employed in the process of nickel-plating. It is obtained by dissolving nickel, free from iron and copper, in dilute sulphuric acid, and adding ammonium sulphate to the concentrated acid solution. The crystalline paste which is deposited is washed with cold water and purified by recrystallisation. It crystallises in short, bluish-green, monoclinic prisms. One hundred parts of water dissolve (Link):

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[1] Phillips and Cooper, *Pogg. Ann.*, 1879, 6, 194.

[2] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1900, 32, 300.

[3] Steele and Johnson, *Journ. Chem. Soc.*, 1904, 85, 113.

[4] Pickering, *ibid.*, 1907, 91, 1985.

At	3·5°	16°	20°	30°	40°	50°	68°	85°	
$(NH_4)_2SO_4,NiSO_4$	1·8	5·8	5·9	8·3	11·5	14·4	18·8	28·6	parts.

The salt is almost insoluble in an acidified solution of ammonium sulphate (Thomson). Many other double sulphates are known,[1] and also a double salt with mercuric cyanide, $NiSO_4,Hg(CN)_2,10H_2O$.[2]

Nickel selenate forms double salts with the alkali selenates. These are of the same type as the double sulphates and isomorphous with them.[3]

NICKEL AND THE ELEMENTS OF THE NITROGEN GROUP, AND BORON.

601 *Nickel Nitride* is obtained by the action of excess of ammonia on metallic nickel at 400–600°, and forms a black powder which readily dissolves in dilute sulphuric and hydrochloric acids.[4] The composition of the product is intermediate between those corresponding to the formulæ Ni_3N and Ni_5N_2. By heating nickelamide at 120° in vacuo, a black, amorphous powder of the nitride, Ni_3N_2, is obtained.[5]

Nickel Azoimide or Azide, $Ni(N_3)_2$, is obtained together with a basic azoimide, N_3NiOH, on treating a nickel salt with azoimide in aqueous solution.[6] It is obtained in the pure state by shaking the dry basic azoimide or finely divided nickel carbonate with azoimide in ethereal solution.[7] It is a sandy, green powder which absorbs water and holds it tenaciously. It is readily soluble in water, but soon hydrolyses in solution. It is extremely explosive and very sensitive even to the slightest rubbing.

Nickelamide, $Ni(NH_2)_2$, is obtained by the action of potassamide on nickel thiocyanate in liquid ammonia.[8] It is a red, flocculent mass which reacts with water, producing nickel hydroxide and ammonia,

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[1] See Tutton, *Phil. Trans.*, 1915, [*A*], **216**, 1.

[2] Scagliarini and Bonini, *Gazz.*, 1920, **50**, [2], 114.

[3] Tutton, *Phil. Trans.*, 1917, [*A*], **217**, 199.

[4] Beilby and Henderson, *Journ. Chem. Soc.*, 1901, **79**, 1251.

[5] Bohart, *J. Physical. Chem.*, 1915, **19**, 537.

[6] Curtius and Rissom, *J. pr. Chem.*, 1898, [2], **58**, 261.

[7] Wöhler and Martin, *Ber.*, 1917, **50**, 586; *Zeit. angew. Chem.*, 1917, **30**, i, 33.

[8] Bohart, *loc. cit.*

$$Ni(NH_2)_2 + 2H_2O = Ni(OH)_2 + 2NH_3.$$

Heated at 120° *in vacuo*, it yields the nitride, Ni_3N_2.

Nitronickel, $Ni_2(NO_2)$, is formed as a black mass mixed with oxide when nitrogen peroxide is passed over reduced nickel, and resembles the corresponding cobalt compounds.[1]

Nickel Nitrite, $Ni(NO_2)_2$, is obtained in solution by the decomposition of the sulphate with barium nitrite. It is a very unstable compound, but forms with potassium nitrite the easily soluble double salt, $4KNO_2,Ni(NO_2)_2$. This is obtained in brownish-red octahedra by mixing a concentrated solution of the nitrite with an excess of potassium nitrite. When potassium nitrite is added to a nickel solution containing a calcium salt, a yellow, crystalline precipitate of $2KNO_2,Ca(NO_2)_2,Ni(NO_2)_2$ is formed, which possesses great similarity to potassium cobaltinitrite (p. 1343), and if a solution contain a sufficient quantity of calcium together with nickel and cobalt, the whole of the nickel, as well as the cobalt, may be thrown down by potassium nitrite. This fact must be remembered in the separation of the two metals. The corresponding barium and strontium compounds have been prepared, and also a number of other double and triple nitrites.[2]

Nickel Nitrate, $Ni(NO_3)_2,6H_2O$, crystallises in green, monoclinic tablets which dissolve in two parts of cold water and in alcohol, and effloresce on exposure to dry air, deliquescing however, in moist air. Hydrates with $3H_2O$ and $9H_2O$ have also been obtained.[3] Anhydrous nickel nitrate is a pale greenish-yellow powder, which begins to evolve nitrous fumes at 105-110°.[4] The tetrammoniate, $Ni(NO_3)_2,4NH_3,H_2O$, is obtained by adding alcohol to a solution of nickel nitrate and ammonia,[5] and the hexammoniate, $Ni(NO_3)_2,6NH_3$, by the action of ammonia on the anhydrous salt.[6] Nickel nitrate forms a number of double nitrates with other nitrates and also a double salt, $Ni(NO_3)_2,Hg(CN)_2,6H_2O$, with mercuric cyanide.[7]

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[1] Sabatier and Senderens, *Bull. Soc. chim.*, 1893, [3], **9**, 669.

[2] Cuttica, *Gazz.*, 1922, **52**, [i], 210.

[3] Funk, *Zeit. anorg. Chem.*, 1899, **20**, 409.

[4] Guntz and Martin, *Bull. Soc. chim.*, 1909, **5**, 1004.

[5] Erdmann, *J. pr. Chem.*, 1840, **19**, 445; see Wyckoff, *J. Amer. Chem. Soc.*, 1922, **44**, 1260.

[6] Ephraim, *Ber.*, 1913, **46**, 3103.

[7] Scagliarini and Bonini, *Gazz.*, 1920, **50**, ii, 114.

Nickel Phosphides.—When nickel and phosphorus are heated in the electric furnace, the compound Ni_2P is obtained in transparent, grey needles of sp. gr. 6·3,[1] insoluble in all acids except a mixture of nitric and hydrofluoric acids. A phosphide of the same composition is prepared in the wet way as a black precipitate by adding nickel chloride to a boiling solution of potash containing some phosphorus and tartaric acid. Compounds of the formulæ P_2Ni_5, P_2Ni_3, P_3Ni_2, PNi_3, P_2Ni, P_3Ni have also been described.[2]

Nickel Arsenides.—These two elements fuse together readily to form brittle alloys, some of which occur as minerals. Of these the most important is kupfer-nickel, niccolite, or nickeline, NiAs, which is found massive, and also, although less frequently, crystallised in hexagonal pyramids. It has a light copper-red colour, and is an important ore of nickel, being found in various localities in Europe and America. Chloanthite, $(Ni,Co,Fe)As_2$, is another nickel arsenide occurring together with the preceding. The study of the freezing-point curve for mixtures of nickel and arsenic indicates the existence of the compounds NiAs, Ni_3As_2, and Ni_5As_2.[3] The diarsenide, $NiAs_2$, has also been obtained.[4]

The Phosphates of Nickel are insoluble in water, and more or less soluble in the mineral acids. The *arsenates* possess similar properties, and some of them occur in the mineral kingdom.

Nickel Boride, NiB, is prepared in the electric furnace from its constituents, and forms brilliant prisms of specific gravity 7·39. It is decomposed by fused alkalis and by water vapour at a dull red heat.[5] The compounds Ni_2B and NiB_2 have also been described.[6] The freezing-point curve of nickel–boron mixtures indicates the formation of the compounds Ni_2B, Ni_3B_2, NiB, and Ni_2B_3.[7]

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[1] Maronneau, *Compt. rend.*, 1900, **130**, 656.

[2] See Granger, *ibid.*, 1896, **122**, 1484; 1896, **123**, 176; Konstantinoff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 742; Jolibois, *Compt. rend.*, 1910, **150**, 106.

[3] Friedrich and Bennigson, *Metallurgie*, 1907, **4**, 200. Compare Vigouroux, *Compt. rend.*, 1908, **147**, 426.

[4] Beutell, *Centr. Min.*, 1916, 49.

[5] Moissan, *Compt. rend.*, 1896, **122**, 424.

[6] Binet du Jassonneix, *ibid.*, 1907, **145**, 240; *Eighth Inter. Cong. App. Chem.*, 1912, **2**, 165.

[7] Giebelhausen, *Zeit. anorg. Chem.*, 1915, **91**, 251.

NICKEL AND THE ELEMENTS OF THE CARBON GROUP.

602 *Nickel Carbide*, Ni_3C.—Carbon dissolves in molten nickel, and the solubility increases with temperature to a maximum at 2100°, which corresponds to the compound Ni_3C. At lower temperatures this dissociates and the decomposition is very rapid at 1600°. Consequently even quenched specimens of the metal contain but little of the carbon in combination and the compound has not been isolated.[1]

Nickel Tetracarbonyl, $Ni(CO)_4$.—When carbon monoxide is passed over metallic nickel at about 350–400°, carbon dioxide is formed and carbon liberated, but at a lower temperature the metal unites with carbon monoxide to form nickel tetracarbonyl. This substance is best prepared by reducing nickel oxide in hydrogen at about 400° in a combustion tube, allowing it to cool to 30–80°, and then passing carbon monoxide over the reduced metal. When the issuing gas is cooled with salt and ice it deposits the nickel carbonyl, the excess of the gas being repeatedly passed over the nickel until no more of the compound is formed. The metal is then again heated in hydrogen at 400°, cooled, and treated with carbon monoxide, the whole process being repeated as often as desired; about 10–15 grams are obtained at each operation.[2] If carbon monoxide under high pressure is employed, the nickel may be heated much more strongly.[3] Thus under 100 atmospheres the nickel carbonyl produced is not decomposed even at 250°.

Nickel tetracarbonyl is a colourless liquid having a specific gravity of 1·3185 at 17°; it boils at 43·2° under 760 mm. pressure, and solidifies at −25°, forming needle-shaped crystals. It has the normal vapour density of 6·01 at 50°, but explodes at 60°, some carbon dioxide being formed and carbon liberated. When diluted with an inert gas the vapour does not explode, and undergoes decomposition less readily;[4] with carbon monoxide as diluent it has nearly the normal vapour density at 100°, and dissociation is not complete at 182°. When gas containing the vapour is passed through a heated tube, pure metallic nickel is deposited with liberation of carbon monoxide.

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[1] Ruff and Martin, *Metallurgie*, 1912, **9**, 143; Ruff, *Ber.*, 1912, **45**, 3139; Ruff and Gersten, *Ber.*, 1913, **46**, 400; Ruff and Bormann, *Zeit. anorg. Chem.*, 1914, **88**, 386; Briner and Senglet, *J. Chim. Phys.*, 1915, **13**, 351.

[2] Mond, Langer, and Quincke, *Journ. Chem. Soc.*, 1890, **57**, 749. See also Tassilly, Pénau and Roux, *Bull. Soc. chim.*, 1921, [4], **29**, 862.

[3] Dewar, *Journ. Chem. Soc.*, 1904, **86**, ii, 468.

[4] Dewar and Jones, *Proc. Roy. Soc.*, 1903, **71**, 427.

It is soluble in alcohol, benzene, chloroform, and carbon tetrachloride. When the solution in benzene is boiled, the carbonyl is decomposed, carbon monoxide being evolved and nickel left as a violet-grey, colloidal solution.[1] Nickel carbonyl is not acted on by dilute aqueous acids or alkalis. It is not decomposed by water free from air, but dissolves to the extent of 18 mgm. per 100 grams of water at 9·8°; dissociation into nickel and carbon monoxide takes place slowly when the solution is preserved. In the presence of air it undergoes oxidation, nickel hydroxide being formed together with a white compound of unknown constitution containing carbon,[2] which may possibly be a basic carbonate.[3] It is rapidly decomposed by the halogens, yielding carbon monoxide and the nickel halide; concentrated sulphuric acid converts it into nickel sulphate with evolution of hydrogen and carbon monoxide, and it is rapidly oxidised by dry concentrated nitric acid. Dry hydrogen chloride and bromide attack it only very slowly, but dry hydrogen iodide yields nickel iodide, hydrogen, and carbon monoxide. With sulphur dissolved in carbon disulphide a sulphide having approximately the composition Ni_2S_3 is formed, whilst sulphuretted hydrogen yields nickel monosulphide.[4] When nickel carbonyl and thiocarbonyl chloride are allowed to react, carbon monosulphide, or a polymeride of this substance, is produced.[5] As already mentioned (p. 1358), the formation and subsequent decomposition of nickel carbonyl are made use of on the large scale in the Mond process for extracting nickel from its ores.

The vapour of nickel tetracarbonyl has a very poisonous action. When inhaled in small quantities it produces toxic symptoms of a very definite type. The lethal dose for men is unknown, but for animals (rabbits, dogs, cats, etc.) it varies between 0·018 and 0·04 volume per cent. of the vapour in air, inhaled for 65 to 90 minutes. The substance is decomposed in the lungs into carbon monoxide and a nickel compound, which is possibly the hydrated basic carbonate. The carbon monoxide available is not sufficient to produce any symptoms, and the toxic effect is entirely due to the nickel content.[6]

[1] Ostwald, *Kolloid Zeit.*, 1914, **15**, 204.

[2] Berthelot, *Compt. rend.*, 1891, **112**, 1343; **113**, 679.

[3] Armit, *Journ. Hygiene*, 1907, **7**, 526.

[4] Dewar and Jones, *Journ. Chem. Soc.*, 1904, **85**, 203.

[5] *Ibid.*, *Proc. Roy. Soc.*, [*A*], 1910, **83**, 408.

[6] Armit, *Journ. Hygiene*, 1907, **7**, 525; 1908, **8**, 565.

Nickel Carbonate, $NiCO_3$, is obtained in the form of pale green, microscopic rhombohedra, by heating nickel chloride solution with calcium carbonate to 150°. When a nickel nitrate solution is mixed with a solution of sodium bicarbonate saturated with carbon dioxide, and this is allowed to stand at a low winter temperature, microscopic, monoclinic crystals of $NiCO_3,6H_2O$ are formed which lose their water readily on warming. A trihydrate, $NiCO_3,3H_2O$, can also be obtained.[1] When a nickel solution is precipitated with an alkali carbonate, basic salts of varying composition are thrown down in the form of pale green precipitates.

Nickel Monocyanide, NiCN.—When a solution of potassium nickelocyanide, $K_2Ni(CN)_4$, is reduced with potassium amalgam in an atmosphere of hydrogen a red solution is obtained containing the salt $K_2Ni(CN)_3$, in which the nickel is monovalent, 2KCN,NiCN. On acidifying the solution, an orange-yellow precipitate is obtained of nickel monocyanide, NiCN, which rapidly oxidises to ordinary nickel cyanide, $Ni(CN)_2$.[2]

The red potassium nickelocyanide, $K_2Ni(CN)_3$, is readily oxidised to the yellow nickelocyanide, $K_2Ni(CN)_4$. This occurs even in absence of air, hydrogen being liberated and metallic nickel deposited:

$$4K_2Ni(CN)_3 + 2H_2O = 3K_2Ni(CN)_4 + Ni + 2KOH + H_2,$$

but in presence of air or of an oxidising agent, such as hydrogen peroxide, nickel hydroxide is precipitated.[3]

$$4K_2Ni(CN)_3 + 2H_2O_2 = 3K_2Ni(CN)_4 + Ni(OH)_2 + 2KOH.$$

With ammonium chloride in the hot, oxidation is very rapid owing to neutralisation of the potassium hydroxide by the acid formed by hydrolysis of the ammonium chloride, and the yellow nickelocyanide formed is further attacked with precipitation of nickel cyanide (Bellucci).

$$K_2Ni(CN)_4 + 2NH_4Cl = Ni(CN)_2 + 2KCl + 2NH_4CN.$$

Nickel Cyanide, $Ni(CN)_2$, is an apple-green precipitate easily soluble in an excess of potassium cyanide with formation of the crystalline double salt, $Ni(CN)_2,2KCN$, or $K_2Ni(CN)_4$.[4] This is again decomposed by dilute acids with separation of nickel cyanide. It is also decomposed by alkaline hypochlorites, a hydrated higher oxide of nickel being precipitated. The corresponding cobalt salt under similar treatment is oxidised to the cobalticyanide which is not further attacked. Advantage is taken of this difference in behaviour for the separation of cobalt and nickel in qualitative analysis. No stable salts corresponding to the ferro- and ferri-cyanides are formed.

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[1] Nanty, *Ann. Chim. Phys.*, 1912, [8], **27**, 5; 1913, [8], **28**, 77.

[2] Bellucci and Corelli, *Atti R. Accad. Lincei*, 1913, [5], **22**, 485.

[3] Bellucci, *Gazz.*, 1919, **49**, ii, 70.

[4] See Rossi, *ibid.*, 1915, **45**, i, 6.

Nickel Silicide, Ni_2Si, is obtained by heating an excess of nickel with silicon in the electric furnace until the greater part of the metal has been volatilised, and then treating the residue with dilute nitric acid. It is a steel-grey, crystalline powder with a metallic appearance, and has the specific gravity 7·2. It is readily attacked by fluorine, and dissolves in hydrofluoric acid and in aqua regia.[1] The method of thermal analysis, controlled by microscopic observations, indicates the existence of the following compounds of nickel and silicon: Ni_3Si, Ni_2Si, Ni_3Si_2, $NiSi$, and Ni_2Si_3.[2]

The *Nickel Silicates* occur in nature. Rewdanskite occurs at Rewdansk in the Urals, and is worked for nickel. It is an earthy mineral which consists chiefly of $(Ni,Fe,Mg)_3Si_2O_7,2H_2O$, and contains about 18 per cent. of nickel. Garnierite, $2(Ni,Mg)_5Si_4O_{13},3H_2O$, occurs in New Caledonia, and is now largely worked up for nickel in France. It contains 24 per cent. of nickel (Liversidge).

The *orthosilicate*, Ni_2SiO_4, is formed in greenish-yellow crystals when the oxide and chloride are heated with amorphous silica.[3]

DETECTION AND ESTIMATION OF NICKEL.

603 Nickel compounds behave in a similar manner to those of iron and cobalt when heated with reducing agents before the blowpipe. An infusible magnetic powder is produced, and when this is dissolved in a drop or two of dilute nitric acid and evaporated to complete dryness, a characteristic green stain is obtained which becomes yellow on further heating. Nickel compounds, moreover, colour the borax bead a brownish-yellow in the oxidising flame, the bead becoming grey and opaque in the reducing flame owing to the separation of metallic nickel.

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[1] Vigouroux, *Compt. rend.*, 1895, **121**, 686; 1906, **142**, 1270.

[2] Guertler and Tammann, *Zeit. anorg. Chem.*, 1906, **49**, 93.

[3] Bourgeois, *Compt. rend.*, 1889, **108**, 1177.

The nickel compounds in general give no flame spectrum, but the acetate when moistened with hydrochloric acid gives first a transient purple, followed by a more permanent deep-red colour, the production of the colour taking place in the inner cone of the flame.[1] The chloride yields a characteristic spark spectrum, and the spectrum of the metal also contains many lines, of which a few of the brightest are 5893 in the orange, and 4874, 4866, and 4856 in the green-blue.

Nickel is very readily detected with the aid of certain organic reagents. Thus when *a*-dimethylglyoxime, $[(CH_3)C:N\cdot OH]_2$, is added to a solution of a nickel salt containing excess of ammonia or of sodium acetate, a scarlet precipitate separates, one part of nickel in 400,000 parts of water being capable of detection in this manner.[2] Cobalt does not give a precipitate with this reagent, nor does it interfere with the reaction unless present in very large excess. This reaction may also be employed for the quantitative estimation of nickel,[3] and, indeed, permits the complete separation of this metal from all other metals belonging to the same analytical group. When dicyanodiamide, $C_2N_4H_4$, and then caustic potash are added to a solution of a nickel salt previously acidified with hydrochloric acid, a dense yellow precipitate is produced of nickel dicyanodiamidine, $Ni(C_2H_5ON_4)_2,2H_2O$, which becomes flesh-coloured when heated. In dilute solutions the precipitate forms only on boiling or standing.[4] *a*-Benzyl dioxime may also be employed for the detection and quantitative estimation of nickel. It gives a red precipitate with nickel salts.[5]

Nickel is precipitated in alkaline solution by ammonium sulphide along with the other metals of the iron group, from all of which except cobalt it can be separated by treating the precipitate with dilute hydrochloric acid, in which the sulphides of these two metals are almost insoluble. A characteristic property of nickel sulphide is that it dissolves slightly in yellow ammonium sulphide to a dark-coloured solution.

The best method for the qualitative detection of nickel and cobalt is based on Liebig's method for their estimation (see below). For this purpose the sulphides are dissolved in concentrated hydrochloric acid with the addition of a crystal of potassium chlorate, and the solution is evaporated nearly to dryness and afterwards diluted with water. Potassium cyanide is then added until the precipitated cyanides re-dissolve, a drop of acetic acid is added and the liquid boiled for a few minutes. The solution then contains potassium cobalticyanide and potassium nickel cyanide. The latter is at once decomposed by sodium hypochlorite in alkaline solution, whereas the former is not attacked by this reagent. The solution is therefore made alkaline with caustic soda and boiled with sodium hypochlorite, when the nickel is precipitated as the black trihydroxide, which may be filtered off, washed, and tested by the borax bead, whilst the cobalt can be detected in the filtrate by evaporating and testing the residue by one of the dry reactions.

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[1] Hartog, *British Assoc. Reports*, 1901, 613.

[2] Tschugaeff, *Ber.*, 1905, **38**, 2520; *Compt. rend.*, 1907, **145**, 679; Brunck, *Zeit. angew. Chem.*, 1907, **20**, 834, 1835.

[3] *Loc. cit.* See also Armit and Harden, *Proc. Roy. Soc.*, 1906, [*B*], **77**, 420.

[4] Grossmann and Schück, *Ber.*, 1906, **39**, 3356; *Chem. Zeit.*, 1907, **31**, 335, 911.

[5] Atack, *Analyst*, 1913, **38**, 316.

Cobalt is much more readily precipitated in the form of sesquioxide than nickel, a fact which is made use of in the commercial separation of the two. This reaction can also be used for the qualitative and quantitative separation of nickel and cobalt. When bromine water is added to a cold neutral solution of the two metals, the cobalt is rapidly precipitated as the sesquioxide, whilst the nickel remains in solution.[1]

Numerous methods, both gravimetric and volumetric, have been proposed for the quantitative separation and estimation of nickel and cobalt. In addition to the dimethylglyoxime and dicyanodiamide processes, already referred to, the three following gravimetric methods may be described.[2]

Liebig's hydrocyanic acid method[3] may be applied to the quantitative separation of the metals substantially in the form which has been described above. The solution containing potassium cobalticyanide and potassium nickel cyanide may be treated with caustic soda and sodium hypochlorite as there described, or may be boiled with precipitated mercuric oxide, the whole of the nickel being precipitated as a mixture of oxides, which after ignition may be weighed as nickel monoxide. The filtrate is acidified with nitric acid, and mercurous nitrate added in excess. Mercurous cobalticyanide is precipitated and is converted by ignition into tricobalt tetroxide. Both in this and the succeeding methods one of the metals is frequently

[1] Taylor, *Mem. Manch. Phil. Soc.*, 1902, **46**, No. 11.

[2] Compare *Zeit. anal. Chem.*, 1891, **30**, 227.

[3] *Annalen*, 1853, **87**, 128.

estimated indirectly. The two are precipitated together by caustic soda from a known volume of solution, and the mixed oxides weighed, the amount of one of the metals being then found by difference.

Another separation of nickel from cobalt depends upon the precipitation of potassium cobaltinitrite (see p. 1343). This is dried at 100° and weighed, and the nickel in the filtrate is precipitated by caustic potash, the precipitate boiled, well washed, and converted by ignition into the monoxide.

A very accurate method depends on the fact that nitroso-β-naphthol, $C_{10}H_6(OH)NO$, yields an insoluble compound with cobalt salts, but not with those of nickel.[1] The solution is therefore acidified with hydrochloric acid, and a solution of this reagent in acetic acid added. A very voluminous precipitate is formed, which is well washed and then ignited with a little oxalic acid, the cobalt being finally heated in hydrogen and weighed.

Nickel may also be estimated by electrolysis of its strongly ammoniacal solution. It may also be estimated by precipitating as oxide (with alkaline hypobromite solution), igniting to the monoxide and weighing as such. Estimation as sulphide may also be made.

The Atomic Weight of nickel has been frequently determined. Of the older determinations, the most important are those of Russell,[2] Schneider,[3] Dumas,[4] Zimmermann,[5] and Winkler.[6] More recent and accurate determinations were made by Richards and Cushman,[7] who deduced the value 58·69 from the amount of silver required to precipitate the bromine in pure nickel bromide, and the value 58·71 from the weight of nickel produced by the reduction of the same compound in hydrogen. Œchsner de Coninck and Gérard [8] by reducing the pure oxalate in hydrogen obtained from the ratio nickel oxalate : hydrogen a value 58·57 as a mean of five determinations. Baxter and Parsons [9] have determined the atomic weight of terrestrial and meteoric nickel by reduction of the oxide in hydrogen. As a mean of nine determinations they find for terrestrial nickel the value 58·70, and as a mean of three determinations for meteoric nickel the value 58·68. The value now adopted (1922) is 58·68.

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[1] Ilinski and Knorre, *Ber.*, 1885, **18**, 699; Chapin, *J. Amer. Chem. Soc.*, 1907, **29**, 1029.

[2] *Journ. Chem. Soc.*, 1863, **16**, 58; *ibid.*, 1869, **22**, 294.

[3] *Pogg. Ann.*, 1857, **101**, 387.

[4] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.

[5] *Annalen*, 1885, **232**, 324.

[6] *Zeit. anal. Chem.*, 1867, **6**, 22; *Zeit. anorg. Chem.*, 1893, **4**, 10, 462; 1895, **8**, 1, 291.

[7] *Zeit. anorg. Chem.*, 1898, **16**, 167; 1899, **20**, 352.

[8] *Compt. rend.*, 1914, **158**, 1345.

[9] *J. Amer. Chem. Soc.*, 1921, **43**, 507.

SUB-GROUP (*b*). THE RUTHENIUM GROUP.

Ruthenium. Rhodium. Palladium.

604 The three metals of this group all have a silvery lustre, combine with oxygen at high temperatures rather more readily than the members of the platinum group, and melt at a lower temperature. The salts of ruthenium and rhodium correspond to the sesquioxide, M_2O_3, whilst palladium forms two series of salts corresponding to the monoxide and dioxide, the former being the more stable. Ruthenium also yields salts of the acidic oxides RuO_3 and Ru_2O_7, and, unlike the other two, forms a tetroxide, RuO_4.

All three metals give rise to series of ammoniacal bases, the properties and composition of which differ, however, in each case. The ruthenium bases all contain the nitroso-group, NO, in addition to ammonia; those of rhodium closely resemble the cobalt derivatives, and those of palladium correspond to two of the series yielded by platinum.

RUTHENIUM. Ru=101·7. At. No. 44.

605 In 1828 Osann[1] stated that he had discovered three new metals in the platinum ores from the Ural. To one of these he gave the name of *ruthenium*, from the name of Russia, the country in which it was found. In the following year, however, he withdrew the statement of the existence of one of the metals, and the existence of the other two remained doubtful until Claus, in 1845, examined the question. This chemist proved the existence of a new metal in the platinum ore, and retained for it the name of ruthenium because it was found to be contained in small quantity in the substance termed ruthenium oxide by Osann, which for the most part consisted of silica, zirconia, and the oxides of titanium and iron. Claus

[1] *Pogg. Ann.*, 1828, **14**, 329; 1845, **64**, 197.

determined the atomic weight of terrestrial and meteoric nickel by reduction of the oxide in hydrogen. As a mean of nine determinations they find for terrestrial nickel the value 58·70, and as a mean of three determinations for meteoric nickel the value 58·68. The value now adopted (1922) is 58·68.

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[1] *Pogg. Ann.*, 1828, **14**, 329; 1845, **64**, 197.

investigated the reactions of the metal and a large number of its derivatives.[1]

Ruthenium is found both in platinum ore and in osmiridium, whilst it occurs as sulphide in laurite, Ru_2S_3.[2]

Of the various methods of preparing the metal, that of Deville and Debray[3] is the most interesting, as these chemists obtained it on a large scale, and specially studied its physical properties. For this purpose, the alloy of osmiridium (p. 1438) containing ruthenium is fused with zinc, the regulus then treated with hydrochloric acid, and one part of the finely-divided residue mixed with three parts of barium peroxide and one part of barium nitrate, the mixture being heated for two hours to a temperature somewhat below the melting point of silver. The cold mass is then reduced to an impalpable powder and thrown into dilute hydrochloric acid contained in a stoppered bottle. In this operation the liquid must be kept well cooled in order to prevent the escape of the poisonous vapours of osmium tetroxide, and the operation must be carried on in a good draught. As soon as the action is over, one part of nitric acid and two parts of sulphuric acid are added to the liquid, the mixture is well shaken, the barium sulphate allowed to deposit, and the clear liquid poured off. The residue is washed by decantation, and the liquid distilled until three-fourths of it has passed over. The distillate is worked up for osmium, whilst the concentrated residue, mixed with from two to three parts of ammonium chloride and a small quantity of nitric acid, is dried on the water-bath. The residue is then washed with water which is half saturated with ammonium chloride, until the filtrate is colourless. By this treatment ammonium iridichloride, containing some ruthenium, remains behind. This is ignited, and the remaining spongy metallic mass fused for two hours in a silver basin with two parts of nitre and one part of caustic potash. The fused mass is then dissolved in water, and the characteristic orange-red solution of potassium ruthenate treated with nitric acid until the yellow colour has disappeared. Ruthenium oxide separates out, but still contains silica, with some iridium and osmium. It is then ignited in a graphite crucible and fused in the oxy-hydrogen furnace.

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[1] *Annalen*, 1845, **56**, 257; 1846, **59**, 234; *Pogg. Ann.*, 1845, **64**, 622; **65**, 200; *Jahresb.*, 1859, 257; 1860, 205; 1861, 230; 1863, 397.

[2] Wöhler, *Annalen*, 1866, **139**, 116.

[3] Deville and Debray, *Compt. rend.*, 1876, **83**, 926; 1879, **89**, 587.

Another plan for preparing chemically pure ruthenium depends upon the fact that whilst osmium tetroxide is volatilised in a stream of air, the corresponding volatile tetroxide of ruthenium is only formed by the action of chlorine in alkaline ruthenium solution. Hence the metal, as obtained by other processes, must be heated in a current of oxygen until the whole of the osmium tetroxide has been volatilised and then fused a second time with potash and saltpetre, the mass dissolved in water, saturated with chlorine, and distilled in a stream of chlorine on the water-bath, when pure ruthenium tetroxide volatilises. This is then dissolved in caustic potash or in water, reduced by alcohol, and the black precipitate converted into metal by ignition in a stream of pure hydrogen.[1]

In order to obtain the metal in the crystalline state it may be fused in a carbon crucible with from five to six times its weight of tin, the alloy being treated with boiling hydrochloric acid, which leaves the compound $RuSn_3$ undissolved; this when ignited in a carbon boat in a current of hydrogen chloride leaves a residue of crystallised ruthenium.

Fused ruthenium has a specific gravity of 12·063 at 0°; like iridium, it is hard and brittle, and next to osmium is the most infusible metal of the group. It can, however, be fused in the oxy-hydrogen flame[2] and distilled in the electric furnace.[3] With the exception of osmium, it is also the one which combines most readily with oxygen, the fused metal becoming covered with a brown film in the air; on cooling it "spits" like silver and iridium. When heated in a current of oxygen it yields the dioxide, and at temperatures of about 1000° some tetroxide also is formed, although this substance decomposes when heated by itself at 107°.[4] The pure metal is scarcely attacked even by aqua regia, but it combines with chlorine at a red heat. *Ruthenium sponge* is made by heating ammonium ruthenichloride.

Colloidal Ruthenium may be prepared by reducing its salts with hydrazine, or other reducing agents, in the presence of a protective colloid such as gum acacia.[5]

[1] See Gutbier and Trenkner, *Zeit. anorg. Chem.*, 1905, **45**, 166.

[2] Mylius and Dietz, *Ber.*, 1898, **31**, 3187.

[3] Moissan, *Compt. rend.*, 1906, **142**, 189.

[4] Debray and Joly, *Ibid.*, 1888, **106**, 100.

[5] Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 452.

RUTHENIUM COMPOUNDS.

Ruthenium and Oxygen.

606 Ruthenium forms the oxides Ru_2O_3, RuO_2, and RuO_4, and, in addition, salts corresponding to the acidic oxides RuO_3 and Ru_2O_7 have been prepared. Oxides of the formulæ RuO, Ru_2O_5, and Ru_4O_9 have also been described, but, according to Gutbier and Ransohoff,[1] these do not exist.

Ruthenium Sesquioxide, Ru_2O_3.—When finely divided ruthenium is heated in the air it combines with 27 per cent. of its weight of oxygen, forming a blue powder which is insoluble in acids. This was regarded by Claus as the sesquioxide, but is more probably a mixture of the dioxide and metal (Gutbier and Ransohoff). The sesquioxide can be obtained, containing a trace of alkali, by heating the trihydroxide in dry carbon dioxide, and forms a black, scaly mass.

Ruthenium Trihydroxide, $Ru(OH)_3$, is obtained by precipitating the corresponding chloride with an alkali. It forms a blackish-brown precipitate, which even after washing with very dilute hydrochloric acid retains a trace of alkali. It dissolves with a yellow colour in acids, but is insoluble in water and alkalis.

The chief ruthenium salts are derived from the sesquioxide, and of these only a few of the halogen compounds are well known. The chloride and its double salts dissolve in water, forming reddish-yellow solutions, which deposit on standing, slowly in the cold but quickly when warmed, a black, very finely divided precipitate of oxychloride. This reaction is so delicate that one part of the metal imparts a distinct ink-like colour to 100,000 parts of water.

Ruthenium Dioxide, RuO_2.—This oxide is obtained by roasting the disulphide or sulphate in contact with air. It is likewise formed if the metal is fused in an oxidising atmosphere, when it burns with a sparkling smoky flame, and evolves an ozone-like smell. Hence this compound can be easily obtained from the ruthenium contained in the osmiridium alloy, which may for this purpose be heated in a porcelain tube to the melting point of copper, in a current of pure air, from which all organic substance has previously been carefully separated. The ruthenium dioxide is carried forward by the osmium tetroxide formed at the same time, and deposited in the cold part of the tube, whilst the more volatile osmium compound is carried on still further by the current of air. The formation of dioxide when the finely divided metal is heated in oxygen begins at 600° and the rate of formation increases very rapidly with rise of temperature.[1] Ruthenium dioxide crystallises in small, very hard, tetragonal pyramids, possessing a green, metallic lustre and a bluish or greenish iridescence. These have a specific gravity of 7·2, and are isomorphous with cassiterite and rutile (Rammelsberg).

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[1] *Zeit. anorg. Chem.*, 1905, **45**, 243, where the literature is quoted.

Ruthenium Tetrahydroxide, $Ru(OH)_4,3H_2O$, is obtained, according to Claus, by evaporating ruthenium disulphate with caustic potash, when a dark red precipitate falls down. The product always contains alkali, and has not been obtained pure. It dries to a reddish-brown mass, giving off water at 300°. When more strongly heated it deflagrates with vivid incandescence and evolution of a black, soot-like smoke. It is soluble in acids and alkalis, yielding yellow solutions.

The oxides RuO_3 and Ru_2O_7 and the corresponding acids have not been prepared, but salts derived from them are known.

Potassium Ruthenate, K_2RuO_4,H_2O, is obtained by igniting a mixture of ruthenium, caustic potash, and potassium nitrate or carbonate, or by the action of 50 grams of the tetroxide on a solution of 70 grams of caustic potash in 500 c.c. of water at 60°; it crystallises from water in rhombic crystals having the above composition, which have a green, metallic reflex, and are red in transmitted light. They take up moisture and carbon dioxide from the air and lose all their water at 200°.

Potassium per-ruthenate, $KRuO_4,H_2O$, is prepared by the action of chlorine on a solution of the foregoing salt, or by dissolving 60 grams of caustic potash in 250 c.c. of water, warming to 60°, and adding 50 grams of ruthenium tetroxide previously fused under water. It forms black, lustrous, tetragonal octahedra. When heated in a vacuum at 400° it decomposes with formation of oxygen, ruthenium dioxide, and the ruthenate, or possibly a salt of potassium with a lower oxide.[2]

Ruthenium Tetroxide, RuO_4.—This compound, as already stated, is formed in small quantity when the metal is heated at 1000° in a current of oxygen, although when heated alone it decomposes at 106—107°. It is prepared by passing chlorine into a solution of potassium nitrosochlororuthenate, or of potassium ruthenate or sodium ruthenate prepared by fusing the metal with sodium peroxide; the liquid becomes heated and the tetroxide distils over and is deposited in the receiver. It is best purified by distillation through anhydrous calcium chloride in a vacuum, the apparatus being carefully freed from organic matter. It melts at 25·5°, the liquid readily remaining superfused, and solidifying to a vitreous mass. When heated it does not boil, but decomposes at 106—107° with a smoky flame but no explosion, the crystalline dioxide being formed. It may, however, be volatilised under reduced pressure, its vapour pressure at 42° and 100·8° being 20 mm. and 183 mm. The vapour has a yellow colour and an irritating odour resembling that of ozone or nitrous fumes. According to Gutbier and Ransohoff, it does not attack the mucous membrane, but cannot long be endured and may produce severe symptoms of poisoning; it blackens organic matter rapidly, and is immediately reduced by alcoholic potash with separation of finely divided metallic ruthenium.[1] Serious explosions may occur if the solid tetroxide is treated with alcohol, even in dilute solution.[2]

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[1] Gutbier and others, *Zeit. anorg. Chem.*, 1916, **95**, 182.

[2] Debray and Joly, *Compt. rend.*, 1889, **108**, 1494; 1891, **112**, 694.

The moist oxide quickly decomposes; in the dry state it is fairly stable, but it decomposes in sunlight with formation of lower oxides. It dissolves slowly in water, and the solution when it contains free chlorine or hypochlorous acid may be kept unchanged for some days in the dark, but when pure slowly deposits a black precipitate. The aqueous solution has a weak acid reaction. Salts are formed with alkali hydroxides but only the ammonium salt, $(NH_4)_2 RuO_5$, has been isolated.[3]

RUTHENIUM AND THE HALOGENS, SULPHUR, AND NITROGEN.

607 Only the trihalogen derivatives of ruthenium have been prepared in the pure state, but it is probable that dihalogen compounds are also formed, and numerous complex substances derived from the tetrahalogen series are known. When chlorine is passed over the metal, combination occurs slowly, but the resulting mass appears to be a mixture.

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[1] Debray and Joly, *Compt. rend.*, 1888, **106**, 328; Joly, *ibid.*, 1891, **113**, 693.

[2] Gutbier and others, *Zeit. anorg. Chem.*, 1916, **95**, 177.

[3] Krauss, *ibid.*, 1921, **119**, 217.

Ruthenium Dichloride, $RuCl_2$, has not been isolated, but is probably present in the blue liquid obtained by the action of sulphuretted hydrogen on a solution of the trichloride.

Ruthenium Trichloride, $RuCl_3$, is said to be formed when the finely divided metal is heated in a mixture of chlorine and carbonic oxide at 360—440° (Joly). It is best prepared by evaporating the tetroxide with hydrochloric acid, chlorine being evolved. It then forms a lustrous mass which dissolves readily in water, forming orange-yellow coloured solutions. The aqueous solution decomposes when gently warmed, an intensely black precipitate being produced (p. 1391).[1] The trichloride unites with ammonia to form a compound, $2RuCl_3,7NH_3$, which forms a deep red solution in water (Joly).

Double salts of the trichloride with alkali chlorides, R_2RuCl_5, known as *rutheniochlorides* or *chlororuthenites*, can easily be obtained.[2] The potassium, rubidium and cæsium compounds are the most characteristic. They form dark-coloured crystals containing $1H_2O$, but the cæsium compound may crystallise anhydrous.[3] An isomeric series of chlorides also exists termed the *aquochlororuthenates*.[4] They are obtained by boiling the solutions of the rutheniochlorides with alcohol. *Potassium aquochlororuthenate*, $K_2Ru(OH_2)Cl_5$, crystallises in rose-red octahedra. Its solution is at once darkened by chlorine.

Ruthenium Tetrachloride, $RuCl_4$, is probably formed when the tetrahydroxide is dissolved in hydrochloric acid, but has not been obtained pure. Its compound with the alkali chlorides and hydrochlorides of organic bases,[5] R_2RuCl_6, known as *ruthenichlorides* or *chlororuthenates*, can readily be obtained.

Potassium Ruthenichloride, K_2RuCl_6, is prepared by fusing ruthenium with potash and potassium chlorate, dissolving in cold water, and adding dilute hydrochloric acid. It forms minute reddish-brown crystals and is sparingly soluble in cold water.[6] The salt formed by the action of chlorine on potassium aquochlororuthenate appears to be isomeric with this (Howe).

Ruthenium Oxychloride, RuO_2Cl_2, is not known, but double alkali salts, such as $RuO_2Cl_2.2CsCl$, have been prepared by the action of hydrochloric acid on the tetroxide in presence of an alkali chloride (Howe).

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[1] Gutbier and Trenkner, *Zeit. anorg. Chem.*, 1905, **45**, 166.

[2] See Miolati and Tagiuri, *Gazz.*, 1900, **30**, ii, 511.

[3] Gutbier, Falco and Vogt, *Zeit. anorg. Chem.*, 1921, **115**, 225.

[4] Howe, *J. Amer. Chem. Soc.*, 1901, **23**, 775; 1904, **26**, 543.

[5] Gutbier and Zwicker, *Ber.*, 1907, **40**, 690; *J. pr. Chem.*, 1915, [2], **91**, 103; Krauss, *Zeit. anorg. Chem.*, 1921, **117**, 111.

[6] Antony and Lucchesi, *Gazz.*, 1899, **29**, ii, 82.

Ruthenium forms also a tribromide and a tri-iodide, and yields series of rutheniobromides and ruthenibromides which closely resemble the chlorine derivatives.[1]

A ruthenium trichloride and tetrachloride and double salts of these with alkali chlorides were described by Claus, but later investigation[2] has shown that these all contain nitrogen, and are in reality nitroso-derivatives.

Ruthenium Sulphide, Ru_2S_3.—This compound occurs as the mineral laurite, which is found with platinum ore in Borneo and Oregon, and usually contains a small percentage of osmium. It crystallises in small octahedra, generally showing also cube faces. Sulphuretted hydrogen gives a precipitate with solutions of ruthenium salts, which consists of a varying mixture of sulphides and oxysulphides of ruthenium with free sulphur.

According to Antony and Lucchesi[3] the precipitate produced in a solution of potassium ruthenichloride, K_2RuCl_6, at 0° is a mixture of the *trisulphide*, RuS_3, and sulphur, whilst at 80° the *disulphide*, RuS_2, is formed. These sulphides become incandescent or explode when gently heated in air.

Ruthenium Sesquisulphite, $Ru_2(SO_3)_3$.—When sulphur dioxide is slowly passed into a solution of ruthenic sulphate, $Ru(SO_4)_2$, the colour changes from bright red through green to blue. Alcohol added to this blue solution produces a blue precipitate of the colloidal sulphite, which may be dried at 80°. It dissolves in water and is precipitated by salts.[4]

Crystalline double salts with the alkali sulphites have been prepared.[5]

Ruthenium Dithionate, RuS_2O_6, is obtained by the continued action of sulphur dioxide on a solution of ruthenic sulphate as a yellow, crystalline, fibrous mass readily soluble in water.[6]

Ruthenic Sulphate, $Ru(SO_4)_2$, is obtained by dissolving the precipitated sulphide in nitric acid, or the tetrahydroxide in sulphuric acid; the reddish-yellow solution leaves on evaporation a yellowish-brown, amorphous mass, which yields a deliquescent powder closely resembling mosaic gold.

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[1] Gutbier and Trenkner, *Zeit. anorg. Chem.*, 1905, **45**, 178; Howe, *J. Amer. Chem. Soc.*, 1904, **26**, 942.

[2] Joly, *Compt. rend.*, 1888, **107**, 994; Howe, *Amer. Chem. J.*, 1894, **16**, 388.

[3] *Gazz.*, 1900, **30**, ii, 539.

[4] Antony and Lucchesi, *Gazz.*, 1900, **30**, ii, 71.

[5] Remy, *Zeit. anorg. Chem.*, 1922, **124**, 248. See also Sailer, *ibid.*, 1921, **116**, 209.

[6] Antony and Lucchesi, *Gazz.*, 1898, **28**, ii, 139.

Ruthenium and Nitrogen.—When brown ruthenium sesquioxide is dissolved in nitric acid it forms a red nitrate; the latter on boiling with successive quantities of hydrochloric acid and evaporation at 120° yields a red, crystalline mass of *ruthenium nitrosochloride*, $RuCl_3NO,H_2O$; on recrystallisation from hot water this forms dichroic triclinic prisms having the composition $RuCl_3NO,5H_2O$, which rapidly effloresce in dry air. It may also be prepared by the action of aqua regia on the tetroxide.[1] This substance combines with alkali chlorides, forming double salts, identical with the substances formerly supposed to be double salts of ruthenium trichloride and the alkali chlorides.[2] The potassium salt has the composition $K_2[RuCl_5(NO)]$, and is a violet-brown, iridescent powder consisting of orange-red, microscopic cubes. In aqueous solution, it yields the ions $2K^{\cdot}$ and $[RuCl_5(NO)]''$, and it is dissociated to about the same extent as potassium platinichloride.[3] Many other similar double salts have also been prepared.

The complex nitroso-derivatives have been investigated by Brizard.[4]

AMMONIACAL DERIVATIVES OF RUTHENIUM.

608 Ruthenium forms a number of derivatives, the basic radicle of which contains both ruthenium and ammonia. These were first examined by Claus, who described a series of salts derived from the hydroxide, $Ru(NH_3)_4(OH)_2$, and also obtained a hydroxide to which he assigned the composition $Ru(NH_3)_2(OH)_2$. According to Joly,[5] however, the salts containing four molecules of ammonia also contain the nitroso-group, and have the general formula $Ru(NH_3)_4(NO)(OH)X_2$, where X is a halogen or monovalent acid radicle, whilst the hydroxide containing two molecules of ammonia is $Ru(NH_3)NO(OH)_3,H_2O$. The salts of the first-named series are well crystallised substances usually of a golden-yellow colour; no crystalline salts have been prepared from the second hydroxide. This has been confirmed by Werner,[6]

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[1] Howe, *J. Amer. Chem. Soc.*, 1894, **16**, 388.

[2] Joly, *Compt. rend.*, 1888, **107**, 994; 1889, **108**, 1300.

[3] Lind, *J. Amer. Chem. Soc.*, 1903, **25**, 928.

[4] *Compt. rend.*, 1899, **129**, 216; *Ann. Chim. Phys.*, 1900, [7], **21**, 311.

[5] *Compt. rend.*, 1889, **108**, 1300; 1890, **111**, 969; 1892, **115**, 1299; Howe, *J. Amer. Chem. Soc.*, 1894, **16**, 388.

[6] *Ber.*, 1907, **40**, 2614.

who regards these compounds as *hydroxynitrosotetrammine-ruthenium salts*, $[Ru(OH)(NO)(NH_3)_4]X_2$, derived from tetravalent ruthenium, and has prepared series of salts in which the hydroxyl group of the complex radicle is replaced by chlorine, bromine, or water, of formula $[Ru(H_2O)(NO)(NH_3)_4]X_3$.

RUTHENIUM AND CARBON AND SILICON.

609 *Ruthenium Carbonyl*, $Ru(CO)_2$, is obtained as a chocolate-brown powder by the action of carbon monoxide on finely divided ruthenium at 300° under a pressure of 400 atmospheres, and is extracted from the residue by solution in alcohol. Unlike all other metallic carbonyls, it is not volatile, is soluble in water and is completely insoluble in benzene. It decomposes on heating, metallic ruthenium being formed.[1]

A volatile, crystalline compound, soluble in benzene, and insoluble in water or alcohol is produced at the same time as the dicarbonyl. Its composition has not yet been determined.

Rutheniocyanides.—These compounds correspond to the ferrocyanides. The *potassium* salt, $K_4[RuCy_6],3H_2O$, is obtained by heating potassium ruthenio-nitrosochloride with potassium cyanide, and forms colourless crystals isomorphous with those of potassium ferrocyanide. Its solution is turned a dark violet colour by ferric salts, and yields a pale green precipitate changing to violet with ferrous salts, whilst the salts of mercury, lead, and zinc yield white precipitates of the corresponding rutheniocyanides.[2] The free *rutheniocyanic acid*, H_4RuCy_6, prepared from the potassium salt by adding hydrochloric acid and extracting with ether, crystallises in pearly laminæ readily soluble in water or alcohol. The solution has an acid reaction and an astringent taste, and on exposure to air turns blue (Claus).

Ruthenium Silicide, RuSi, is formed in small, white crystals when the elements are heated together in the electric furnace. It has the specific gravity 5·40, and is very hard. It is not attacked by boiling acids, but is decomposed by the halogens; it burns in oxygen, and yields a per-ruthenate when fused with potassium hydrogen sulphate and potassium nitrate.[3]

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[1] Mond, *Rep. British Assoc.*, 1915, 393; *J. Chim. Soc.*, 1910, **97**, 798; Mond and Wallis, *Journ. Chem. Soc.*, 1921, **121**, 29.

[2] See Howe, *J. Amer. Chem. Soc.*, 1896, **18**, 981; Howe and Campbell, *ibid.*, 1898, **20**, 29.

[3] Moissan and Manchot, *Compt. rend.*, 1903, **137**, 229.

DETECTION AND ESTIMATION OF RUTHENIUM.

610 The ruthenic salts give a dark red precipitate with concentrated solutions of potassium chloride and ammonium chloride; on boiling with water the characteristic ruthenium oxychloride is formed. Ruthenium solutions are first coloured blue by sulphuretted hydrogen, and afterwards the brown sulphide is formed, almost insoluble in ammonium sulphide. The production of the volatile tetroxide is also characteristic.

Ruthenium, like the other members of this group, is estimated quantitatively as the metal.

Atomic Weight of Ruthenium.—Claus[1] first determined this constant, but the later investigations of Joly[2] with carefully purified material have shown that the figures of Claus are too high. Joly determined the atomic weight (1) by reducing the dioxide in hydrogen; (2) by the reduction of the nitrosochloride in hydrogen; (3) by the reduction of ammonium nitrosochlororuthenate, the numbers obtained being respectively 101·67, 101·74, and 101·62, and the atomic weight is therefore at present (1922) taken as 101·7.

RHODIUM. Rh=102·9. At. No. 45.

611 When Wollaston[3] in 1804 first acknowledged that he was the discoverer of palladium (p. 1407), he likewise intimated that he had found another new metal in platinum ore, to which he gave the name of rhodium, because the solutions of its salt possess a rose-red colour (ῥόδον, a rose). The metal and its compounds were later investigated by Berzelius and Claus. In addition to its occurrence in platinum ore, rhodium had been found, according to Del Rio, alloyed with gold as rhodium-gold.

In order to prepare rhodium from the mixed platinum metals, the solution is employed from which ammonium platinichloride has been precipitated. The metals still in solution are then precipitated by metallic iron, and, according to the process of Deville and Debray, the metallic precipitate is fused with one part of lead and two parts of litharge. A regulus is thus obtained, from which the lead, copper, and palladium may be dissolved out by the action of dilute nitric acid. The insoluble metallic powder is then well mixed with five parts of barium peroxide and heated to redness for two hours, the solid mass being lixiviated with water, and the residue boiled with aqua regia in order to volatilise the osmium tetroxide, this latter being condensed. The excess of barium is precipitated from the solution by sulphuric acid, the filtrate evaporated at 100° with an excess of ammonium chloride, and the residue washed with a solution of the same salt as long as the wash-water has a rose-red colour. The filtrate is then evaporated with an excess of nitric acid in order to decompose the ammonium chloride, and the residual mass heated to redness with from three to four parts of sulphur. It is then rapidly boiled out with aqua regia and sulphuric acid, and by this treatment nearly pure rhodium remains behind. In order further to purify this, it is fused with from three to four parts of zinc, and the alloy treated with strong hydrochloric acid, when the compound $RhZn_2$ remains behind. This is dissolved in aqua regia and evaporated with an excess of ammonia. Rhodammonium chloride, $Rh(NH_3)_5Cl_3$, separates out, and this is then purified from traces of iridium by recrystallisation, and ignited in a carbon crucible with some sulphur, and, lastly, in order to remove from it any traces of silicon and osmium, fused in the oxy-hydrogen or electric furnace.

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[1] *Petersb. Akad. Bull.*, **3**, 353.

[2] Joly, *Compt. rend.*, 1889, **108**, 946.

[3] *Phil. Trans.*, 1804, **94**, 419.

Another method of preparing the pure metal is that described by Bunsen,[1] for the particulars of which his memoir on the subject must be consulted. He obtained from one kilogram of the platinum residues from the St. Petersburg mint 33·2 grams of pure rhodium sodium sulphate, $Na_3Rh(SO_4)_3$.

Commercial rhodium frequently contains iridium. If, however, the metals are converted into the chloropentammine chlorides, the rhodium salt may be obtained quite free from iridium by treating the mixture with nitric acid, filtering off the chloropentamminerhodium nitrate which crystallises out, and reconverting this into the chloride, which then yields rhodium quite free from iridium.[2]

Rhodium can also be obtained free from iridium when the latter is present as an iridic salt such as $Ir(SO_4)_2$, by precipitating the mixed salts with caustic potash, dissolving the hydroxides in dilute sulphuric acid, and adding cæsium sulphate. The sparingly soluble rhodium cæsium alum separates in the cold, and can readily be purified by recrystallisation and then decomposed electrolytically.[1]

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[1] *Phil. Mag.*, 1868, [4], **36**, 253.

[2] Jörgensen, *Zeit. anorg. Chem.*, 1903, **34**, 82. See also Mylius and Dietz, *Ber.*, 1898, **31**, 3187; Leidié, *Compt. rend.*, 1900, **131**, 888; Leidié and Quennessen, *Bull. Soc. chim.*, 1901, [3], **25**, 840.

Properties.—Rhodium possesses the colour and lustre of aluminium, and has a specific gravity of 12·1. It fuses with greater difficulty than platinum, its melting point being 1907°. It is less volatile than platinum,[2] and, unlike iridium, reduces the volatility of this metal when alloyed with it. Such alloys are therefore preferable for the manufacture of crucibles.[3] When the metal is heated in air or in oxygen, the sesquioxide is formed, but decomposes again at temperatures above 1150°.[4] The molten metal "spits" on cooling, the surface becoming coloured blue from oxidation; it can be distilled in the electric furnace.[5]

Pure rhodium, as well as that which contains gold and platinum, is almost insoluble in acids. If, however, it be alloyed with bismuth, zinc, lead, or copper, it dissolves in aqua regia. Alloys of much platinum and little rhodium also dissolve in aqua regia, but if the rhodium be present in larger quantity much remains undissolved. Rhodium can, however be brought into solution by repeated ignition with fused potassium hydrogen sulphate, as well as with phosphoric acid or acid phosphates. Of all the platinum metals, rhodium is the most easily attacked by chlorine.[6]

Rhodium Black.—When a solution of one of its salts is heated with sodium formate, the metal is precipitated in the form of a fine black powder. It evolves considerable quantities of carbon dioxide, hydrogen, and oxygen, together with other gases and water when heated *in vacuo*.[7] It is an active catalyst, and brings about the union of hydrogen and oxygen in a similar manner to platinum black.[8] It possesses the property of decomposing formic acid, with evolution of heat, into hydrogen and carbon dioxide. After a time the action becomes weaker, but the powder then simply requires to be washed with water and dried in the air to be again rendered active.[1] At a somewhat higher temperature, and in presence of caustic potash, it also decomposes alcohol, with evolution of hydrogen and formation of potassium acetate; it does not lose this power at a temperature at which glass begins to soften (Deville and Debray).

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[1] Piccini and Marino, *Zeit. anorg. Chem.*, 1901, **27**, 62.

[2] Crookes, *Proc. Roy. Soc.*, 1912, **86**, 461.

[3] Burgess and Sale, *J. Ind. Eng. Chem.*, 1914, **6**, 452; 1915, **7**, 516; Burgess and Waltenburg, *ibid.*, 1916, **8**, 487.

[4] Gutbier, Hüttlinger, and Maisch, *Zeit. anorg. Chem.*, 1916, **95**, 225.

[5] Moissan, *Compt. rend.*, 1906, **142**, 189.

[6] Gutbier and Hüttlinger, *Zeit. anorg. Chem.*, 1916, **95**, 247.

[7] Sieverts and Jurisch, *Ber*, 1912, **45**, 221.

[8] Quennessen, *Compt. rend.*, 1904, **139**, 795; *Bull. Soc. chim.*, 1905, [3], **33**, 191.

Colloidal Rhodium.—An unstable, colloidal solution of rhodium can be obtained by Bredig's method,[2] which consists in sparking between electrodes of rhodium under water, or by reducing the pure chloride with hydrazine hydrate. In presence of gum arabic, the solution can be evaporated over sulphuric acid, and yields a dark brown residue which contains 99·4 per cent. of rhodium and is almost completely soluble in warm water.[3] Other protective colloids, such as sodium protalbate or lysalbate, may also be employed,[4] and the best method of preparing the colloid consists in reducing sodium rhodochloride by formaldehyde in the presence of one of these.[5] Colloidal rhodium absorbs hydrogen to the extent of more than 2,500 times the volume of rhodium present, and carbon monoxide to the extent of 350 times its volume at ordinary temperatures and 1,800 times at 60°. It causes a slight union of nitrogen and hydrogen to form ammonia,[5] and decomposes hydrogen peroxide, the reaction being unimolecular as in the case of platinum.[6]

Alloys.—Rhodium combines with tin, yielding the alloy $RhSn_3$, which forms small, brilliant crystals.[7] It forms also a bismuth compound, $RhBi_4$, which crystallises in needles and is completely soluble in aqua regia;[8] it appears to form a compound with gold, but not with silver. The alloy with platinum containing 10 per cent. of rhodium is largely used in the form of wire in the construction of thermo-electric pyrometers.

Crucibles and other forms of chemical apparatus are now made of malleable rhodium, and it is essential to use the perfectly pure metal for their preparation (Matthey).

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[1] Blackadder, *Zeit. physikal. Chem.*, 1912, **81**, 385.

[2] Lancien, *Compt. rend.*, 1911, **153**, 1088.

[3] Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 452.

[4] Paal and Amberger, *Ber.*, 1904, **37**, 124.

[5] Zenghelis and Papaconstantinou, *Compt. rend.*, 1920, **170**, 1058.

[6] *Ibid.*, 1920, **170**, 1178.

[7] Debray, *ibid.*, 1887, **104**, 1470.

[8] Rössler, *Chem. Zeit.*, 1900, **24**, 733.

RHODIUM COMPOUNDS.

RHODIUM AND OXYGEN.

612 Rhodium forms three oxides, RhO, Rh_2O_3, and RhO_2.

Rhodium Monoxide, RhO, is obtained by heating the trihydroxide, $Rh(OH)_3$, by the cupellation of an alloy of rhodium and lead, or by igniting the finely divided metal in a current of air. It is a grey, metallic powder, unattacked by acids; when heated in hydrogen it is reduced with evolution of light.

Rhodium Sesquioxide, Rh_2O_3, is obtained as a grey, iridescent, spongy mass by heating the nitrate. It is also formed as a crystalline mass when sodium rhodochloride is heated in oxygen. It is insoluble in acids.

Rhodium Trihydroxide, $Rh(OH)_3$, is a black, gelatinous precipitate, obtained by heating a solution of sodium rhodochloride with excess of caustic potash. On drying it forms a heavy, dark brown mass having a conchoidal fracture and a metallic lustre. It is scarcely attacked by acids.

If a solution of the sodium double chloride be treated in the cold with potash not in excess, it becomes opaque, and on long standing deposits thin, lemon-yellow crystals of the hydroxide, $Rh(OH)_3,H_2O$, which dissolve readily in acids, and, when moist, in caustic potash. When chlorine is passed into the solution of the yellow hydroxide in caustic potash, a blue coloration is produced,[1] which is probably due to the formation of a perrhodate, Na_2RhO_4.

The rhodium salts are derived from the sesquioxide. They possess either a dark red or a yellow colour, and have a bitter but not astringent taste.

Rhodium Dioxide, RhO_2, is obtained by repeated fusion of the metal with caustic potash and saltpetre. The sesquioxide is first formed, and is further oxidised. It closely resembles the sesquioxide; it is not attacked by alkalis or acids, and is reduced by hydrogen only at a high temperature.

Rhodium Tetrahydroxide, $Rh(OH)_4$.—When chlorine is passed into the alkaline solution of the sesquihydroxide for a long time, and caustic potash occasionally added, this compound separates out as a green powder, the liquid becoming blue or violet. The green powder dissolves in hydrochloric acid to a blue solution; this colour gradually changes to dark red, chlorine being evolved. The violet-blue solution probably contains the potassium salt of a rhodous acid, which latter separates out after some time as a blue powder, gas being simultaneously evolved. On drying, it is converted into the tetrahydroxide.

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[1] See Alvarez, *Compt. rend.*, 1905, **140**, 1341.

Insoluble crystalline salts of the composition $K_2O,6RhO_2$, $Na_2O,8RhO_2$, and $BaO,12RhO_2$ are obtained when the corresponding double nitrites are heated *in vacuo* and the products treated with water. These substances may be regarded as *rhodites*, analogous to the manganites, cobaltites, and chromites.[1]

613 *Rhodium Trichloride*, $RhCl_3$, is obtained by the continued ignition of the finely divided metal in chlorine, and also by heating one of the alkali double salts with sulphuric acid and pouring the cooled mixture into water; a rose-red powder of insoluble rhodium chloride remains behind. It may be convienently prepared from the crude double chloride, $RhCl_3,3NaCl$, obtained by the action of chlorine on the metal in presence of sodium chloride, by dissolving it in water, precipitating the sodium chloride by hydrochloric acid, evaporating, and heating the residue in a current of chlorine or hydrogen chloride. It then forms a brown powder, insoluble in water or acids, but soluble in alkalis and in potassium cyanide.[2] It is obtained also as a brick-red powder by heating the rhodium tin alloy, $RhSn_3$, in chlorine at 440°, the tin volatilising as stannic chloride. When the yellow hydroxide is dissolved in hydrochloric acid, a yellow solution is obtained possessing an astringent taste, which on concentration becomes rose red, and then possesses the peculiar bitter taste characteristic of all rhodium salts. When this solution is evaporated, a dark red, amorphous mass of the hydrated chloride is obtained, which is deliquescent, and on further heating yields the insoluble anhydrous chloride.

The trichloride yields a large number of well-crystallised *rhodochlorides* or *chlororhodites*. The *sodium* salt, $Na_3RhCl_6,9H_2O$, crystallises in deep cherry-red, triclinic prisms, which are very soluble in water, and effloresce in the air to a peach-blossom coloured powder. The *ammonium* salt, $2(NH_4)_3RhCl_6,3H_2O$, forms four-sided, rhombic prisms.

The dark salt formed with potassium chloride has the formula $2KCl,RhCl_3$ or K_2RhCl_5. It crystallises in dark red, acicular prisms which contain $1H_2O$, according to Berzelius, but according to Leidié are anhydrous. Another hydrate, $K_2RhCl_6,3H_2O$, crystallising in dark red prisms has been described by Claus.

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[1] Leidié, *Compt. rend.*, 1899, **129**, 1249.

[2] Joly and Leidié, *ibid.*, 1896, **27**, 103.

Rhodium Monosulphide, RhS.—When rhodium is heated in sulphur vapour it takes fire with formation of the sulphide, which is produced also when sulphuretted hydrogen is passed through a solution of a rhodium salt, and the washed precipitate dried by ignition in a current of carbon dioxide. Thus obtained, it forms a bluish-white, fused mass of metallic lustre; heated in the air it leaves a residue of spongy rhodium.

Rhodium Sesquisulphide, Rh_2S_3, is obtained in the pure state by heating the trichloride in sulphuretted hydrogen at 360°, and forms blackish, crystalline plates. The *hydrosulphide*, $Rh(SH)_3$, is precipitated when sulphuretted hydrogen in large excess is passed into a solution of a rhodium salt at 100°, and forms a brownish-black precipitate which is insoluble in ammonium sulphide.[1]

Rhodium Sulphite, $Rh_2(SO_3)_3,6H_2O$, is obtained by dissolving the yellow hydroxide in sulphurous acid and evaporating. It is a pale yellow, indistinctly crystalline mass, and forms crystalline double salts.

Rhodium Sulphate, $Rh_2(SO_4)_3,12H_2O$, is obtained by dissolving the yellow hydroxide in sulphuric acid, evaporating, and washing away the excess of acid by alcohol. It is a yellow, crystalline mass which possesses a sour, astringent taste. The anhydrous salt is a brick-red, non-hygroscopic powder (Leidié). According to Claus, it forms crystalline double salts with the alkali sulphates, but Leidié was unable to confirm this statement.

A series of *rhodium alums* of the alkali metals, ammonium, and thallium has been prepared by dissolving the yellow hydroxide in excess of dilute sulphuric acid and adding two-thirds of the calculated amount of the alkali sulphate.[2] *Rhodium cæsium alum*, $Cs_2SO_4,Rh_2(SO_4)_3,24H_2O$, forms yellow octahedra, melts at 110—111°, and is sparingly soluble in cold water. The potassium compound, on the other hand, is extremely soluble in water, the rubidium and ammonium salts being intermediate in solubility.

Rhodium Nitrite, $Rh(NO_2)_3$, has not been isolated, but forms characteristic double salts. *Sodium rhodium nitrite*, $3NaNO_2,Rh(NO_2)_3$, separates in bulky, white crystals, which act on polarised light. The *potassium* salt also forms white, microscopic crystals when pure,[1] but is usually obtained as a heavy, orange-coloured, crystalline powder, which dissolves readily in hydrochloric acid.

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[1] Leidié, *Compt. rend.*, 1888, **106**, 1533.

[2] Piccini and Marino, *Zeit. anorg. Chem.*, 1901, **27**, 62.

Rhodium Nitrate, $Rh(NO_3)_3$, does not crystallise, but forms a dark yellow, hygroscopic, gummy mass.

Potassium Rhodicyanide, $K_3[RhCy_6]$, is obtained in a similar way to the corresponding iridium salt (p. 1447), which it closely resembles. It may also be prepared by dissolving the yellow hydroxide in caustic potash, diluting, and adding to an excess of hydrocyanic acid.[2] It is distinguished from the iridium salt, inasmuch as acetic acid produces a pale crimson-red precipitate of *rhodium cyanide*, $RhCy_3$, soluble in the cyanides of the alkali metals, forming the rhodicyanides (Martius).

AMMONIACAL DERIVATIVES OF RHODIUM.

614 The ammoniacal rhodium bases and salts closely resemble the corresponding cobalt compounds. The three chief series have the following general formulæ:

Hexammine salts (Luteo-salts) $[Rh(NH_3)_6]X_3$
Aquopentammine salts (Roseo-salts) $[Rh(H_2O)(NH_3)_5]X_3$.
Pentammine salts (Purpureo-salts) $[RhX(NH_3)_5]X_2$

in which X is a monovalent negative radicle.

Hexammine-Rhodium Trichloride (*Luteorhodium Chloride*), $[Rh(NH_3)_6]Cl_3$, is obtained in colourless, lustrous crystals by heating the salt next described with ammonia.

Chloropentammine-Rhodium Dichloride (*Chloropurpureorhodium Chloride*), $[RhCl(NH_3)_5]Cl_2$, is prepared by dissolving the alloy of rhodium and zinc in aqua regia and adding ammonia. It forms small, yellowish, lustrous, rhombic crystals.

Aquopentammine-Rhodium Chloride (*Roseorhodium Chloride*), $[Rh(H_2O)(NH_3)_5]Cl_3,H_2O$, is obtained by digesting the foregoing compound with silver oxide for several days, and dissolving the resulting base in hydrochloric acid.

Optically Active Rhodium Ammine Salts.—There is considerable similarity between rhodium and cobalt salts. The triethylenediamine cobalt salts form optical isomerides, and Werner has succeeded in obtaining the optical isomerides of triethylenediaminerhodium salts.[3]

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[1] Leidié, *Compt. rend.*, 1890, **111**, 106.

[2] *Ibid.*, 1900, **130**, 87.

[3] *Ber.*, 1912, **45**, 1228.

DETECTION AND ESTIMATION OF RHODIUM.

615 Solutions of this metal are precipitated by sulphuretted hydrogen, slowly in the cold, but more quickly when warmed. The brown sulphide is insoluble in ammonium sulphide. When a rhodium compound is heated in hydrogen the metal is obtained; this is insoluble in aqua regia, but can be obtained in solution when it is fused with acid potassium sulphate. The fused mass on treatment with water yields a red solution, from which the metal is precipitated as a black powder on addition of caustic potash and alcohol. It is also precipitated from acid solution by zinc and other metals.

Rhodium is estimated quantitatively as the metal.

Atomic Weight of Rhodium.—Jörgensen,[1] from the analysis of chloropentamminerhodium dichloride and of the analogous dibromide, obtained the number 103·1, and Seubert and Hobbe,[2] by the same method, the number 102·94. This figure has been confirmed by the later work of Hüttlinger,[3] who found, as a mean of three determinations, the value 102·93, and Dittmar,[4] who, as a mean of seven experiments, obtained the figure 102·91. The value now adopted (1922) is 102·9.

PALLADIUM. Pd = 106·7. At. No. 46.

616 In April, 1803, a printed notice came[5] into the hands of Chenevix, to the effect that a new metal, called Palladium, was to be sold at Forster's, of Gerrard Street, Soho. Chenevix,[6] believing that this was simply a fraud, bought the whole stock,

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[1] *J. pr. Chem.*, 1883, [2], **27**, 486.

[2] *Annalen*, 1891, **260**, 314.

[3] *Sitzungsber. phys. med. Soz. Erlangen*, 1907, **39**, 1.

[4] *Ibid.*, 1909, **40**, 184.

[5] "Palladium, or new silver, has these propeties amongst others that show it to be a new noble metal:—1. It dissolves in pure spirit of nitre, and makes a dark red solution. 2. Green vitriol throws it down in the state of a regulus from this solution, as it always does gold from aqua regia. 3. If you evaporate the solution you get a red calx that dissolves in spirit of salt or other acids. 4. It is thrown down by quicksilver, and by all the metals but gold, platinum, and silver. 5. Its specific gravity by hammering was only 11·3; but by flattening as much as 11·8. 6. In a common fire the face of it tarnishes a little and turns blue, but comes bright again, like other noble metals, on being stronger heated. 7. The greatest heat of a blacksmith's fire would hardly melt it. 8. But if you touch it while hot with a small bit of sulphur, it runs as easily as zinc."

[6] *Phil. Trans.*, 1803, **93**, 290.

and after investigating the question he came to the conclusion that the substance was not a new metal, but that it was a platinum amalgam of peculiar properties. Soon after the communication of Chenevix's paper to the Royal Society (May 13, 1803), an advertisement appeared in which a handsome reward was offered to any one who should prepare even a grain of this substance, either according to Chenevix's plan, or by any other method. No one succeeded in obtaining the reward, although several German chemists endeavoured to prepare the new substance. In 1804 Wollaston[1] declared that he was the discoverer of palladium, having taken this name from that of a new planet Pallas, discovered by Olbers in 1802. At the same time he described the process which he adopted in order to obtain the new metal from platinum ore.

Palladium occurs in a tolerably pure state with Brazilian platinum ore, as well as together with gold, at Tilkerode, in the Harz. It is contained in most platinum ores, and is found in many places in South America alloyed with gold.

Numerous methods of separating palladium from the other platinum metals have been described. Among these may be mentioned the precipitation of the dicyanide by the addition of mercuric cyanide to a neutral solution of a palladium salt, and the treatment of the dichloride solution with potassium iodide, or freshly precipitated silver iodide,[2] which yields palladious iodide as a black, insoluble precipitate. The cyanide is converted into the metal by ignition, and the iodide by heating in a current of hydrogen. Bunsen,[3] by the iodide method, prepared pure palladium from the platinum residues of the St. Petersburg mint, which consisted of a mixture of all the platinum metals. Other methods of working up the platinum metals on the large scale have been given by Philipp,[4] Guyard,[5] and Leidié.[6] From the palladium-gold alloy it may be obtained by fusing the latter with silver, and treating the granulated metal with moderately dilute nitric acid, which dissolves the silver and palladium, but leaves the gold unattacked. The silver is precipitated with sodium chloride, and the palladium from the filtrate by metallic zinc.[7]

To prepare pure palladium from the commercial metal, it is dissolved in aqua regia, and precipitated as the double ammonium chloride together with platinum and other metals. The precipitate is treated with excess of ammonia, when the palladium salt dissolves, and on addition of hydrochloric acid yields, after a time, a precipitate of yellow palladdiammonium chloride. This sometimes contains rhodammonium chloride, which is separated by retreatment with ammonia and addition of hydrochloric acid. The washed precipitate yields spongy palladium on ignition.

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[1] *Phil. Trans.*, 1804, **94**, 428; 1805, **95**, 316.

[2] Orloff, *Chem. Zeit.*, 1906, **30**, 714.

[3] *Phil. Mag.*, 1868, [4], **36**, 253.

[4] *Dingl. Polyt. Journ.*, 1876, **220**, 95.

[5] *Compt. rend.*, 1863, **56**, 1177.

[6] *Ibid.*, 1900, **131**, 858.

[7] Cook, *Phil. Mag.*, 1843, [3], **23**, 16.

Palladium has a colour closely resembling that of silver and platinum, a specific gravity of 11·4 at 22·5° (Deville and Debray), or 11·9 (Mylius and Dietz);[1] it melts at 1549°, the lowest melting point of all the platinum metals. At the melting point of iridium it boils violently, with partial oxidation, and emits green vapours, which condense to a brown sublimate consisting of a mixture of oxide and metal.[2]

Palladium is dimorphous. The native metal occurs in the Brazils in the form of sand or rounded grains, amongst which small, regular octahedra are sometimes found. Native palladium usually contains small quantities of both platinum and iridium, and has a specific gravity varying from 11·3 to 11·8. The palladium found in the Harz occurs in small, hexagonal tablets, together with gold and lead selenide, and hence this latter body was first considered to be palladium selenide. Owing to the difference of crystalline form this variety has been termed by Danna[3] *Allopalladium*.

When palladium is heated to dark redness it assumes a violet or blue colour, but at higher temperatures it regains its metallic lustre, and this remains even when the metal is quickly cooled by plunging into water. When heated in a current of oxygen till the weight is constant it forms the monoxide, PdO.[4] Palladium dissolves readily in nitric acid, especially when this contains nitrous acid, or when the metal is alloyed with either copper or silver. It also dissolves in hydrochloric acid if chlorine be passed into the liquid, and is attacked by boiling concentrated sulphuric acid, and by fused potassium bisulphate.

617. *Palladium and Hydrogen*.—Palladium is distinguished for its remarkable power of absorbing or occluding hydrogen.

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[1] *Ber.*, 1898, **31**, 3187.

[2] See also Moissan, *Compt. rend.*, 1906, **142**, 189.

[3] *Mineralogy*, 5th ed., p. 12.

[4] Wilm, *Ber.*, 1892, **25**, 220; Wöhler, *Zeit. Elektrochem.*, 1905, **11**, 836.

This property was first discovered by Graham,[1] who observed that absorption of hydrogen occurred when the gas was passed over metallic palladium which had been heated to redness, or when the metal was employed as the negative electrode in the electrolysis of water. He found that the metal absorbed about 900 times its own volume of hydrogen, termed the occluded gas *hydrogenium*, and thought it was present in the solid state. The absorption or occlusion of hydrogen by palladium has since been the subject of many investigations. Sieverts[2] found that the quantity of hydrogen absorbed is independent of the superficial area of the metal and concluded that the phenomenon is a case of simple solution. At constant temperature, the amount absorbed is very nearly proportional to the square root of the pressure of the hydrogen. With increase of temperature, the amount absorbed decreases rapidly to 600°, then slowly to 800°, and then only very slightly. At the melting point, the molten metal absorbs less hydrogen than the solid, consequently there is no "spitting" when molten palladium solidifies in an atmosphere of hydrogen.[2] The whole of the occluded gas can be removed by heating *in vacuo* even at 100°.[3] The rate of occlusion of hydrogen falls off in proportion to the amount of gas already absorbed, and it is therefore probable that the process of occlusion is first simple adsorption on the surface layer, followed by slow diffusion into the interior of the metal from this layer.[4] From the rate of cooling of palladium in hydrogen, Andrew and Holt[5] conclude that the metal exists in two allotropic modifications and the absorption of hydrogen may be regarded as taking place rapidly in the one form and more slowly in the other, thus accounting for the initial rapidity and subsequent slowness of the occlusion.[6]

The physical properties of palladium undergo considerable change through the absorption of hydrogen. The specific gravity of palladium-hydrogen is less than that of the metal, hence expansion must occur in the formation of the compound. This expansion can be shown in several ways. One of the most striking is to fit two palladium wires horizontally through the edges of a thin electrolytic trough with parallel glass sides. The trough is then filled with acidulated water, and an image of the wires thrown on a screen. An electric current is now passed through the cell, when a singular bending of the palladium wire from which the hydrogen is evolved is noticed. If the current be reversed this wire first returns to its original horizontal position, and then bends to the opposite side, whilst the other wire is deflected in the former direction, the explanation of this double bending being that first one side, and then the other side of the wire becomes saturated with, or loses the hydrogen.[1] If one side of a piece of palladium foil be saturated electrolytically with hydrogen, then washed and dried, and afterwards ignited, it becomes so bent that it has almost the appearance of having been rolled up into a coil.

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[1] *Phil. Mag.*, 1866, **32**, 516; *Proc. Roy. Soc.*, 1867, **15**, 223; 1868, **16**, 422; 1869, **17**, 212, 500.

[2] *Zeit. physikal. Chem.*, 1914, **88**, 103, 451.

[3] Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, 1897, **62**, 290.

[4] Holt, Edgar, and Firth, *Zeit. physikal. Chem.*, 1913, **82**, 513.

[5] *Proc. Roy. Soc.*, 1913, [*A*], **89**, 170.

[6] Holt, *ibid.*, 1914, [*A.*], **90**, 226; Firth, *Journ. Chem. Soc.*, 1920, **117**, 171.

The electrical conductivity of palladium decreases with occlusion of hydrogen. It first decreases proportionately to the amount of hydrogen absorbed up to 40 volumes, then asymptotically up to 600 volumes and then proportionately again. This break in the rate of decrease of conductivity is attributed to the formation of a compound, PdH_2.[2] The formation of another hydride, Pd_2H, had been assumed by other investigators[3] from a study of the pressure of the hydrogen evolved from hydrogenated palladium at different temperatures, but the existence of this compound has not been confirmed.[4] The magnetic susceptibility of palladium is also decreased by the absorption of hydrogen.[5]

The occluded hydrogen is chemically very active. The product containing hydrogen often becomes heated on exposure to the air from absorption of oxygen and formation of water, and when palladium black has been employed this action may be sufficiently vigorous to render the powder pyrophoric (Paal and Amberger). Palladium foil charged with hydrogen acts as an excellent reducing agent, reducing ferric and ceric salts, ferricyanides, and chromates, and may be employed for this purpose in quantitative analysis.[6]

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[1] Poggendorff, *Ber.*, 1869, **2**, 74. See also Dewar, *Phil. Mag.*, 1887, [4], **47**, 334.

[2] Wolf, *Zeit. physikal. Chem.*, 1914, **87**, 575.

[3] Troost and Hautefeuille, *Compt. rend.*, 1874, **78**, 686.

[4] Hoitsema, *Zeit. physikal. Chem.*, 1895, **17**, 1.

[5] Biggs, *Phil. Mag.*, 1916, [6], **32**, 131; Oxley, *Proc. Roy. Soc.*, 1922, [*A*], **101**, 264.

[6] Chapman, *Analyst*, 1904, **29**, 346.

The power of palladium to absorb hydrogen is diminished by certain substances, notably hydrogen sulphide and lead salts. The question has been studied by Maxted, and the decrease in occlusive power is found to be approximately proportional to the amount of "poison" present.[1] The occlusive power of palladium is greatly affected by alloying it with other metals. Thus the solubility of hydrogen in palladium is increased by the presence of silver, although hydrogen is insoluble in silver. The increase in solubility continues with increase in the amount of silver up to a maximum at 40% of silver, when the solubility at 138° is four times as great as in pure palladium. Further increase of the silver content results in a decrease in solubility, and at 70% of silver the solubility is reduced to zero. Addition of gold, in the same way, causes first an increase and then a decrease in the occlusive power, but the effect is not so marked. Platinum, on the other hand, decreases the solubility when alloyed with palladium in any proportions. Unlike the other cases, the solubility here increases with rise of temperature. With all the alloys the solubility is proportional to the square root of the pressure of the hydrogen, as in the case of pure palladium.[2]

Palladium also occludes other gases, notably carbon dioxide.[3]

Hydrogen readily diffuses through palladium, the metal exhibiting this property, also, in a very much more marked degree than platinum or iron. The rate of diffusion is approximately proportional to the pressure of the gas.[4] The diffusion of hydrogen is selective; for example, pure hydrogen diffuses through the metal from ordinary coal gas.[5] Hydrogen which has been ionised by *X*-rays or radium does not diffuse through palladium.[6]

Spongy Palladium.—On heating ammonium palladiochloride decomposes, ammonium chloride being evolved and the palladium left in a spongy form. In this condition the metal is more active. It dissolves in hydrochloric acid in presence of air and absorbs hydrogen very readily. The arrangement shown in Fig. 201 is that proposed by Wöhler[7] for exhibiting the decomposition of palladium-hydrogen by heat and the reabsorption of the hydrogen on cooling. The U-tube (*a*) dipping in boiling water contains the spongy palladium, over which a current of hydrogen is passed for half an hour from the cylindrical generator on the right of the figure. The water-bath is then removed, and the tube allowed to cool in the current of hydrogen. The stopcock (*d*) is now shut, and the tube (*a*) placed in communication with the tube (*b*). This latter dips in the cylinder and is bent up at the lower end into the tube (*c*). The tube (*a*) is next heated with a flame, when the cylinder soon becomes filled with hydrogen, and on allowing the spongy metal to cool, a rapid absorption of the hydrogen occurs. The experiments can be repeated as often as desired.

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[1] Maxted, *Journ. Chem. Soc.*, 1919, **115**, 1050; 1920, **117**, 1280, 1601; 1921, **119**, 1281.

[2] Sieverts, Jurisch, and Metz, *Zeit. anorg. Chem.*, 1915, **92**, 329; Tammann, *Zeit. anorg. Chem.*, 1920, **111**, 90.

[3] Harbeck and Lunge, *ibid.*, 1898, **16**, 50.

[4] Holt, *Proc. Roy. Soc.*, 1915, [*A*], **91**, 148.

[5] Graham, *loc. cit.*; Ramsay, *Phil. Mag.*, 1894, **38**, 206.

[6] Sieverts, *Zeit. physikal. Chem.*, 1914, **88**, 103.

[7] *Annalen*, 1876, **184**, 128.

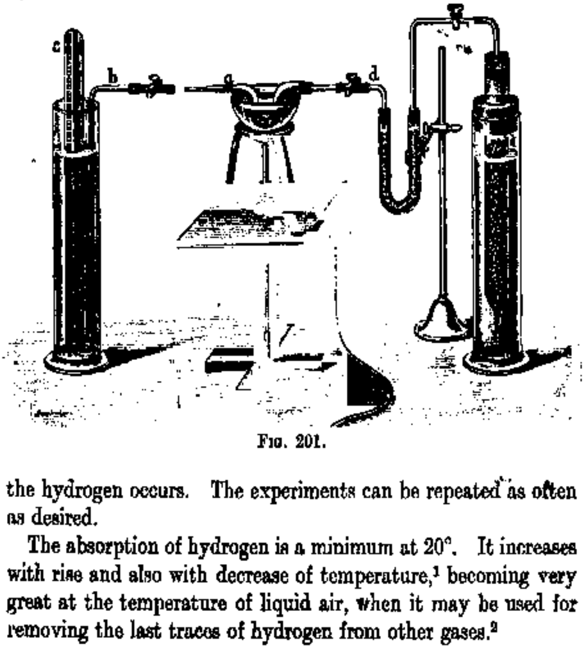

Fig. 201.

The absorption of hydrogen is a minimum at 20°. It increases with rise and also with decrease of temperature,[1] becoming very great at the temperature of liquid air, when it may be used for removing the last traces of hydrogen from other gases.[2]

Palladium Black is obtained, similarly to platinum black, by reduction of palladium salts with soldium formate. Owing to its affinity for oxygen, it contains some palladious oxide.[3] It absorbs hydrogen very readily, but on heating the occlusive power is diminished. The black is regarded as a mixture of amorphous and crystalline palladium, and on heating the amorphous is converted into the crystalline variety, in which hydrogen is less soluble. All forms of palladium have the same capacity for absorbing hydrogen above 600°. The absorption is probably a case of simple adsorption in the amorphous metal, but of true solution in the crystalline variety. Palladium black is gradually converted into palladium sponge by heat.[1]

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[1] Gutbier, Gebhardt, and Ottenstein, *Ber.*, 1913, **46**, 1453.

[2] Valentiner, *Ber. Deut. physikal. Ges.*, 1911, **13**, 1003.

[3] Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, 1897, **62**, 50.

Palladium in all its forms acts as a catalyst in many reactions.[2] When warm palladium foil is brought into an electrolytic mixture of hydrogen and oxygen, or other explosive gaseous mixture, combination takes place without explosion (Coquillon),[3] and when the metal is brought into the flame of alcohol or coal gas it becomes covered with a thick film of soot. When palladium sponge is placed in a current of ethylene, this gas is decomposed with separation of carbon; this occurs at a temperature at which the gas alone does not undergo any alteration.[4]

In the presence of the finely divided metal at moderate temperatures, hydrocarbons mixed with air are completely burnt to carbon dioxide and water. Sodium hypophosphite solution is readily oxidised first to the phosphite and then, more slowly, to the phosphate, with evolution of hydrogen.[5]

Colloidal Palladium.—A colloidal solution of palladium can be prepared by the electrical method,[6] by the action of formaldehyde, hydrazine hydrate,[7] or carbon monoxide[8] on palladious chloride, and by the action of hydrazine hydrate or gaseous hydrogen on a palladium salt in presence of sodium protalbate.[9] The last preparation can be obtained by evaporation as a solid hydrosol, which absorbs hydrogen. It dissolves readily in water yielding the colloidal solution again.

Colloidal palladium is an exceptionally active catalyst. Like platinum, it decomposes hydrogen peroxide and catalyses reductions by hydrogen,[1] in most cases to a more marked degree. Nitrobenzene is readily reduced to aniline,[2] unsaturated compounds are readily saturated, partially or wholly, and many oils may be "hardened" as when nickel is used as catalyst. This activity is doubtless connected with the power of the colloid to absorb hydrogen. It also absorbs acetylene to a most remarkable degree, about 5000 volumes of this gas being dissolved, doubtless owing to the formation of condensation and polymerisation compounds.[3]

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[1] Sieverts, *Zeit. physikal. Chem.*, 1914, **88**, 103; Firth, *Journ. Chem. Soc.*, 1921, **119**, 1120.

[2] Lunge and Akunoff, *Zeit. anorg. Chem.*, 1900, **24**, 191; Zelinsky, *Ber.*, 1898, **31**, 3203.

[3] *Compt. rend.*, 1876, **83**, 709. See also Tammann, *Zeit. anorg. Chem.*, 1920, **111**, 90.

[4] Wöhler, *Annalen*, 1876, **184**, 128.

[5] Sieverts and Peters, *Zeit. physikal. Chem.*, 1916, **91**, 199.

[6] Bredig and Fortner, *Ber.*, 1904, **37**, 798.

[7] Gutbier, *Zeit. anorg. Chem.*, 1902, **32**, 347; Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 358.

[8] Donau, *Monatsh.*, 1906, **27**, 71.

[9] Paal and Amberger, *Ber.*, 1904, **37**, 124; 1905, **38**, 1398; Amberger, *Kolloid Zeit.* 1913, **13**, 310.

The colloid is readily poisoned by many substances, notably hydrogen sulphide, hydrogen cyanide, hydrogen arsenide, and mercuric salts. It readily converts mercury and mercuric oxide into colloidal solution, and thus loses its activity, probably owing to the formation of a colloidal amalgam.[4] Mercury, in fact, decomposes palladium-hydrogen hydrosols with evolution of hydrogen.[5] The catalytic activity of palladium hydrosols first increases with age, reaches a maximum, and then decreases again.[6]

Palladium is now employed in preference to platinum in dentistry for the production of artificial teeth, and also in jewellery, particularly for the setting of stones. On account of its unalterability in the air, and owing to its bright silver-white colour, it has been employed for the preparation of graduated surfaces for astronomical instruments. It is likewise used for coating silver goods, as palladium does not lose its fine white colour on exposure to sulphuretted hydrogen, and hence it has been much employed by dentists as a substitute for gold also. Spongy palladium is used in gas analysis to absorb hydrogen.

Palladium alloys with gold,[7] silver,[7] copper,[7] and nickel[8] in all proportions no compounds being formed. It also alloys with lead, forming a series of compounds.[9] The alloys with gold have a high melting point, and are so resistant to corrosion that they are, for many purposes, employed as a substitute for platinum, and are known as *Rhotanium*.[1] Palladium also forms an amalgam which may be made by rubbing the finely divided metal with mercury.

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[1] Kelber and Schwarz, *Ber.*, 1912, **45**, 1946; Böeseken, van der Weide, and Mom, *Rec. trav. chim.*, 1916, **35**, 260; Berti-Ceroni, *Gazz.*, 1916, **46**, ii, 51; Nivière, *Bull. Soc. chim.*, 1921, [4], **29**, 217; Sandonnini and Quaglia, *Gazz.*, 1922, **52**, i, 409.

[2] Paal and Amberger, *Ber.*, 1905, **38**, 1406.

[3] Paal and Hohenegger, *Ber.*, 1910, **43**, 2684; 1915, **48**, 275; Paal and Schwarz, *ibid.*, 1915, **48**, 1195.

[4] Paal and Hartmann, *Ber.*, 1918, **51**, 711, 894.

[5] Paal and Steyer, *ibid.*, 1918, **51**, 1743.

[6] De Rocasolano, *Compt. rend.*, 1920, **171**, 301.

[7] Ruer, *Zeit. anorg. Chem.*, 1906, **51**, 223, 315.

[8] Heinrich, *ibid.*, 1913, **83**, 322.

[9] Tammann, *ibid.*, 1921, **118**, 93.

PALLADIUM COMPOUNDS.

PALLADIUM AND OXYGEN.

618. Three oxides of palladium are known: the monoxide, PdO, the sesquioxide, which has only been obtained in the hydrated condition, Pd_2O_3,xH_2O, and the dioxide, PdO_2. A suboxide, Pd_2O, has also been described,[2] but it is probable that this is in reality a mixture of the metal and the monoxide.[3]

Palladium Monoxide, PdO, is formed by the long-continued heating of the spongy metal in a current of oxygen at temperatures rising from 700–840°, or by heating a mixture of a palladium salt with potassium carbonate. Prepared in the first manner it is a bluish-green, and by the second an amber-coloured mass, which yields a black powder. On strong ignition, it yields the metal, the dissociation pressure[4] being 760 mm. at 877°, and it is reduced by hydrogen at the ordinary temperature with evolution of light and heat. It acts as a powerful oxidising agent to organic substances, and is reduced to metal by hydrogen peroxide. If a palladious salt be precipitated with sodium carbonate, a dark brown hydroxide, readily soluble in acids, is thrown down, whilst the anhydrous oxide dissolves only after long boiling. When precipitated in the cold it is soluble in alkalis, but loses this property when dried or when prepared from a boiling solution. The pure hydrated oxide is best prepared by the hydrolysis of the nitrate.

The palladious salts, corresponding to this oxide, possess a green, red, or brown colour, and have an astringent, but not metallic, taste.

Palladium Sesquioxide is obtained in the hydrated condition by the electrolytic oxidation of palladious nitrate.[5] It forms a brown precipitate which dissolves readily in hydrochloric acid, forming an unstable chloride. Palladium is thus brought more into line with its neighbours rhodium and ruthenium.

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[1] Fahrenwald, *J. Ind. Eng. Chem.*, 1917, **9**, 590; Gurevich and Wichers, *ibid.*, 1919, **11**, 570.

[2] Kane, *Phil. Trans.*, 1842, **132**, 276; Neumann, *Monatsh.*, 1892, **13**, 40.

[3] Wöhler and König, *Zeit. anorg. Chem.*, 1905, **46**, 323.

[4] Wöhler, *Zeit. Elektrochem.*, 1905, **11**, 836; 1906, **12**, 781.

[5] Wöhler and Martin, *Zeit. anorg. Chem.*, 1908, **57**, 398.

Palladium Dioxide is obtained in an impure hydrated form as a brown precipitate by the addition of caustic soda to potassium palladichloride. This is soluble in acids, but becomes less soluble when preserved. It can be obtained free from alkali and basic salts by the anodic oxidation of the nitrate, but is not quite free from monoxide. The dioxide very readily decomposes into the monoxide and oxygen, and cannot be obtained in the anhydrous state. It acts as a vigorous oxidising agent, and decomposes hydrogen peroxide (Wöhler and König).

PALLADIUM SALTS.

619. *Palladious Chloride*, $PdCl_2$, is obtained by heating palladious sulphide, PdS, in dry chlorine, when it is obtained partly as a rose-red sublimate and partly in the form of garnet-red crystals which dissolve slowly but completely in water. It is prepared in solution by the simultaneous action of chlorine and hydrochloric acid on the metal. On evaporation over caustic lime, brown-red crystals having the composition $PdCl_2,2H_2O$ are deposited. These lose water when gently heated, the anhydrous chloride remaining as a brownish-black mass which melts easily without decomposition, and is reduced by hydrogen in the cold. At a red heat it fuses and loses half of its chlorine, forming the *monochloride*, PdCl, which, on cooling, solidifies to a reddish-brown, crystalline mass yielding a light red powder which is very deliquescent. The aqueous solution partially decomposes with separation of basic salts, and the solution is reduced by hydrogen, carbon monoxide, and other gases.[1] When heated, palladious chloride unites with carbon monoxide,[2] forming the crystalline compounds, $PdCl_2,2CO$, melting at 142°, $2PdCl_2,3CO$, melting at 132°, and $PdCl_2,CO$. These substances are analogous to the corresponding platinum compounds.

Palladious chloride forms double chlorides with other chlorides, known as *palladiochlorides* or *chloropalladites*.[3] A large number of these salts of organic bases have been prepared.[4]

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[1] Böttger, *J. pr. Chem.*, 1859, **76**, 233.

[2] Fink, *Compt. rend.*, 1898, **126**, 946.

[3] See Gutbier and Krell, *Ber.*, 1905, **38**, 2385.

[4] Gutbier, *Ber.*, 1905, **38**, 2105; *Zeit. anorg. Chem.*, 1905, **47**, 23; Gutbier and Krell, *Ber.*, 1905, **38**, 3800; 1906, **39**, 616, 1292; Gutbier and Woernle, *Ber.*, 1906, **39**, 2716; Gutbier, Fellner, and others, *Zeit. anorg. Chem.*, 1916, **95**, 129.

Potassium Palladiochloride, K_2PdCl_4, is obtained by adding potassium chloride to a solution of palladious chloride. It may also be prepared by ignition of potassium palladichloride. It is easily soluble in water, less so in alcohol, and crystallises in four-sided prisms, exhibiting a red-green dichroism.

Ammonium Palladiochloride, $(NH_4)_2PdCl_4$, is obtained by evaporating a solution of palladium chloride with ammonium chloride. It forms either bronze-yellow prisms exhibiting a play of different colours, or yellowish-green needles, and dissolves in water, forming a dark-red solution.

Palladic Chloride, $PdCl_4$, is not known in the free state. The brown solution obtained by dissolving the metal in concentrated aqua regia contains *palladichloric* or *chloropalladic acid*, H_2PdCl_6, corresponding to chloroplatinic acid; this forms salts with the alkali metals and certain aromatic bases.[1]

Potassium Palladichloride, K_2PdCl_6, is obtained by adding potassium chloride to a solution of the metal in an excess of aqua regia and gently evaporating. It is also prepared by precipitating a solution of palladious chloride, saturated with chlorine, with an excess of potassium chloride, or by warming the palladiochloride with potassium persulphate and hydrochloric acid.[2] It forms cinnabar-red or brownish-red octahedra showing the faces of the cube. These dissolve in hot dilute hydrochloric acid without decomposition, but are not soluble in water containing the chlorides of the alkali metals, or in alcohol.

Ammonium Palladichloride $(NH_4)_2PdCl_6$, is a bright-red, crystalline powder consisting of microscopic octahedra. It is obtained by precipitating a solution of the chloride, saturated with chlorine, by ammonium chloride. On treating the solution with an excess of ammonia a violent evolution of nitrogen takes place, ammonium palladiochloride being formed:

$$3(NH_4)_2PdCl_6 + 2NH_3 = 3(NH_4)_2PdCl_4 + 6HCl + N_2.$$

Palladious Bromide, $PdBr_2$, is obtained by treating the metal with bromine hydrate and nitric acid, and forms a chestnut-brown mass which dissolves in hydrobromic acid but not in water.

Potassium palladiobromide, K_2PdBr_4, crystallises in lustrous, reddish-brown needles which are stable in the air. Many analogous salts are known (Gutbier and Krell).

Palladic Bromide, $PdBr_4$, is not known, but the *palladi-*

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[1] Möhlau, *Ber.*, 1906, **39**, 861.

[2] Scagliarini and Berti-Ceroni, *Gazz.*, 1916, [2], **46**, 51.

bromides of the alkali metals, R_2PdBr_6, have been prepared by passing bromine vapour into the solutions of the corresponding palladiobromides. They are sparingly soluble salts which are decomposed by hot water and by ammonia (Gutbier and Krell).

Palladious Iodide, PdI_2, is obtained by precipitating the chloride with potassium iodide as a black, flocculent precipitate which, when dried in the air, forms a deliquescent mass exhibiting a conchoidal fracture. It dissolves slowly in hydriodic acid and readily in a solution of potassium iodide, imparting to this a wine-red colour. When heated to 100° it begins to give off iodine, and it decomposes completely at temperatures between 330° and 360°. The solution in potassium iodide yields on evaporation blackish-green, deliquescent cubes of *potassium palladioiodide*, K_2PdI_4.

Palladium Subsulphide, Pd_2S, is obtained by fusing ammonium palladiochloride with sodium carbonate, sulphur, and ammonium chloride. A green, molten mass is thus obtained which crystallises on cooling and exhibits a metallic fracture. It is only slowly attacked by aqua regia.

Palladium Monosulphide, PdS, is formed with incandescence when the metal is heated in the vapour of sulphur. It is a bluish-white, hard mass, which exhibits a laminated fracture and a metallic lustre, and oxidises only slowly in the air. A black precipitate is formed by passing sulphuretted hydrogen through a solution of a palladious salt; this is generally supposed to be palladious sulphide, but it always contains more sulphur than is required by the formula PdS.[1]

Palladium Disulphide, PdS_2.—When the foregoing compound is fused with sodium carbonate and sulphur, *sodium thiopalladate*, Na_2PdS_3, is formed. This crystallises in reddish-brown needles having a slightly metallic lustre. It is decomposed by hydrochloric acid with formation of the disulphide, which is a crystalline, dark brown powder easily soluble in aqua regia. When heated in carbon dioxide it is first converted into the monosulphide, and at a higher temperature into the subsulphide.

A salt of the formula $(NH_4)_2PdS_{11},\frac{1}{2}H_2O$ crystallises slowly in slender, yellowish-red needles when solutions of ammonium polysulphide and potassium palladiochloride are mixed.[2]

Sodium Palladiosulphite, $Na_6[Pd(SO_3)_4],2H_2O$, is obtained as a white, crystalline precipitate by adding caustic soda to a solution of the chloride which has been saturated with sulphur dioxide. The simple sulphite is not known.

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[1] Petrenko-Kritschenko, *Zeit. anorg. Chem.*, 1893, 4, 247.

[2] Hofmann and Höchtlen, *Ber.*, 1904, 37, 245.

Palladious Sulphate, $PdSO_4,H_2O$, is obtained by dissolving the hydroxide in sulphuric acid, or by dissolving the metal in the same solvent with the addition of nitric acid. It forms indistinct olive-green, deliquescent crystals which are decomposed by water with formation of a basic salt, $PdSO_4,7Pd(OH)_2$, as a brown insoluble powder.

Potassium Palladionitrite, $K_2[Pd(NO_2)_4]$, is obtained on addition of potassium nitrite to a hot solution of potassium palladiochloride as a pale yellow, crystalline powder, the production of which serves as a microchemical test for palladium.[1] The simple nitrite is not known.

Numerous complex nitrites, sulphites, phosphates, and oxalates have also been described.[2]

Palladious Nitrate, $Pd(NO_3)_2$, is formed by dissolving the metal or the oxide in nitric acid. It crystallises in long, brownish-yellow, deliquescent, rhombic prisms which probably contain water of crystallisation. A brown powder, $Pd(NO_3)_2,3Pd(OH)_2$, is formed on the addition of water to the solution.

Palladious Cyanide, $PdCy_2$, is obtained as a pale yellow precipitate on addition of mercuric cyanide solution to a solution of palladious salt, which must contain no free acid and should not be too dilute. On solution in potassium cyanide and evaporation, transparent, thin, rhombic prisms of *potassium palladiocyanide*, $K_2[PdCy_4],3H_2O$, or small tablets containing $1H_2O$ are obtained. The cyanide is also soluble in acids and in ammonia, and the latter solution yields needles or pearly scales of *palladodiammine cyanide*, $[Pd(NH_3)_2Cy_2]$.

Palladious Thiocyanate, $Pd(SCy)_2$ is a reddish, flocculent precipitate, and dissolves in potassium thiocyanate solution, forming *potassium palladiothiocyanate*, $K_2[Pd(SCy)_4]$, which crystallises in ruby-red needles.[3]

Palladium Silicide.—When palladium and silicon are fused together they unite, and the melting-point curve shows the formation of the compounds Pd_2Si and $PdSi$. By dissolving out the silicon with dilute potash from any alloy containing more than 60% Si, the latter compound is obtained as bluish-grey fragments of specific gravity 7·31.[1]

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[1] Pozzi-Escot and Conquet, *Compt. rend.*, 1900, 130, 1073.

[2] Rosenheim and Itzig, *Zeit. anorg. Chem.*, 1900, 23, 28; Vezes, *Bull. Soc. chim.*, 1899, [3], 21, 172; Loiseleur, *Compt. rend.*, 1900, 131, 262; Finck, *ibid.*, 1896, 123, 603.

[3] Bellucci, *Atti R. Accad. Lincei*, 1904, [5], 13, ii, 386.

Ammoniacal Palladium Compounds.

620. These have been investigated chiefly by Hugo Müller,[2] and are formed by the action of ammonia on palladious salts. They appear to belong to two series:

Palladosammine compounds, $[Pd(NH_3)_2X_2]$,
Palladodiammine compounds, $[Pd(NH_3)_4]X_2$,

and are analogous to the corresponding platinum compounds. Unstable hydroxylamine derivatives have also been prepared which probably belong to the same two series.[3]

An extended investigation of the palladosammine salts in which ammonia is replaced by organic nitrogen bases has been carried out by Gutbier and his colleagues.[4]

In addition to these, pyridine derivatives of the type $[Pd(Py)_2Cl_2]Cl_2$, derived from tetravalent palladium, have been described.[5]

Palladosammine Hydroxide, $[(OH)_2(NH_3)_2Pd]$, is obtained by the decomposition of the sulphate with baryta water, or of the chloride with silver oxide and water. The yellow solution thus obtained, when dried over sulphuric acid, yields a crystalline, ochre-yellow mass. The solution has all the properties of a solution of an alkali hydroxide.

Dichlorodiammine Palladium or *Palladosammine Choride*, $[Cl_2(NH_3)_2Pd]$, is obtained by the addition of an excess of ammonia to palladious chloride and either evaporating, or, better, precipitating the salt by means of hydrochloric acid. It forms fine, yellow needles, which consist of contiguous octahedra and is almost insoluble in water.

Tetramminepalladious Hydroxide or *Palladodiammine Hydroxide*, $[(NH_3)_4Pd](OH)_2$, is obtained by the decomposition of the sulphate with baryta. It is a colourless, crystalline mass; its aqueous solution has a strong alkaline reaction, precipitates the salts of copper, iron, cobalt, nickel, and aluminium, but not those of silver, and decomposes ammoniacal salts.

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[1] Lebeau and Jolibois, *Compt. rend.*, 1908, **146**, 1028.

[2] *Annalen*, 1853, **86**, 341.

[3] Zeisel and Nowack, *Annalen*, 1907, **351**, 439.

[4] *Ber.*, 1905, **38**, 2107, 3869; 1906, **39**, 610, 1292, 2716; *Zeit. anorg. Chem.*, 1905, **47**, 23. See also Hardin, *J. Amer. Chem. Soc.*, 1899, **21**, 943.

[5] Rosenheim and Maas, *Zeit. anorg. Chem.*, 1898, **18**, 331.

Tetramminepalladious Chloride or *Palladodiammine Chloride*, $[(NH_3)_4Pd]Cl_2$, is formed by the repeated evaporation of palladious chloride with ammonia. It crystallises in large, colourless, four-sided, monoclinic prisms easily soluble in water.

Vauquelin's salt, $[Pd(NH_3)_4]Cl_2,PdCl_2$, is obtained by the action of a slight excess of ammonia on palladious chloride.

DETECTION AND ESTIMATION OF PALLADIUM.

621. The two most characteristic reactions of palladium are (1) the precipitation of its hydrochloric acid solution by potassium cyanide, the yellowish-white palladium cyanide being thrown down, soluble in both hydrochloric acid and ammonia; and (2) the production of a black precipitate of palladious iodide, insoluble in hydrochloric acid, when potassium iodide or freshly precipitated silver iodide is added to a palladium solution. By these reactions it may be separated from all metals, with the exception of copper, and this may be previously removed, according to Wöhler, by precipitation as cuprous thiocyanate, after saturation with sulphur dioxide.

Palladium is estimated gravimetrically as the metal, obtained by the ignition of the cyanide or by the reduction of the salts with a hydrazine salt[1] in acid solution.[2] Palladium may be estimated also by precipitating with acetylene and igniting the precipitate,[3] and by weighing the metal deposited electrolytically with a rotating anode.[4] A very convenient method of estimating palladium, especially in the presence of nickel, is based on the fact that in acid solution it is quantitatively precipitated by dimethyl glyoxime. The yellow-orange precipitate is filtered, washed, and ignited to the metal. On neutralising the filtrate, any nickel present is at once precipitated as the red glyoxime compound.[5] Palladium may also be precipitated from acid solution by α-nitroso-β-naphthol in a similar manner to cobalt. The red precipitate is filtered, washed, and ignited to the metal. This method is particularly useful because the other platinum metals are not precipitated by this reagent; moreover, owing to the intense red of the compound it affords a delicate test for palladium, even 0·001 gram per litre being easily diluted.[1]

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[1] Jannasch and Bettges, *Ber.*, 1904, **37**, 2210.

[2] Jannasch and Rostosky, *Ber.*, 1904, **37**, 2441; Paal and Amberger, *Ber.*, 1905, **38**, 1388.

[3] Erdmann and Makowka, *Ber.*, 1904, **37**, 2694.

[4] Amberg, *Zeit. Elektrochem.*, 1904, **10**, 385.

[5] Wunder and Thuringer, *Ann. Chim. anal.*, 1912, **17**, 201.

Atomic Weight of Palladium.—Until the year 1889 the only determination of the atomic weight of palladium was that of Berzelius, who obtained the number 106 by the analysis of potassium palladiochloride. Since 1889 the atomic weight has been redetermined by several investigators, but the results vary considerably. Keiser[2] by the determination of the palladium in palladosammine chloride found the number 106·5, and by the same method, using very carefully purified material, Keiser and Breed[3] found the value 106·47. Bailey and Lamb,[4] by the same method, found the number 105·7, and a value closely agreeing with this, 105·8, was obtained by Joly and Leidié[5] by the analysis of potassium palladiochloride. Keller and Smith[6] from the electrolytic determination of the metal in palladosammine chloride obtained the much higher number 107·1. A high figure, 106·99, was also obtained by Hardin,[7] who estimated the metal in diphenylpalladodiammonium chloride, $Pd[NH_2(C_6H_5)Cl]_2$, and the corresponding bromide, and in ammonium palladiobromide. On the other hand, Amberg[8] has obtained a lower number, 106·64, by the analysis of palladosammine chloride, the chlorine and the metal being both estimated. Shinn[9] reduced the double chloride of palladium and ammonium with formic acid, and found as the mean of nine experiments the figure 106·71. The most probable value is (1922) taken as 106·7.

SUB-GROUP (*c*). THE PLATINUM GROUP.

Osmium. Iridium. Platinum.

622 These metals are distinguished by their high specific gravity and melting point. Osmium alone forms a tetroxide, thus resembling ruthenium.

The tendency to form complex salts is exceedingly strongly marked, and with the exception of the sulphides and halogen derivatives, very few simple salts are known. Such as are known have the general formulæ MR_2, MR_3, and MR_4, corresponding to the basic oxides MO, M_2O_3, and MO_2, but the series MR_3 is scarcely represented among the platinum compounds. The most important of the series of the complex salts are the halogen acids and their derivatives, such as K_2PtCl_4, K_3IrCl_6, and K_2OsCl_6, the complex nitrites, such as $K_3Ir(NO_2)_6$ and $K_2Pt(NO_2)_4$, the complex cyanides and thiocyanates, such as $K_2Pt(CN)_4$ and $K_2Pt(SCN)_4$, the sulphites, and above all the ammoniacal derivatives.

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[1] Schmidt, *Zeit. anorg. Chem.*, 1913, **80**, 335.

[2] *Amer. Chem. J.*, 1889, **11**, 398.

[3] *Ibid.*, 1894, **16**, 20.

[4] *Journ. Chem. Soc.*, 1892, **61**, 745.

[5] *Compt. rend.*, 1893, **116**, 146.

[6] *Amer. J. Sci.*, 1892, **44**, 423.

[7] *J. Amer. Chem. Soc.*, 1899, **21**, 943.

[8] *Annalen*, 1905, **341**, 235.

[9] *J. Amer. Chem. Soc.*, 1912, **34**, 1448. Compare Gutbier, Haas, and Gebhardt, *J. pr. Chem.*, 1909, **79**, 457.

OSMIUM. Os = 190·9. At. No. 76.

623 In 1803 Smithson Tennant investigated the metallic residue which remains when platinum ores are dissolved, and this he believed to contain a new metal. At the same time Descotils, as well as Fourcroy and Vauquelin, came to the conclusion that the solution contained a peculiar metal. However, in 1804 Tennant[1] proved that the platinum residues contained two new metals, to one of which he gave the name of iridium, on account of the varying colour of its salts, and to the other the name osmium (ὀσμή, a smell), because of the peculiar odour of its volatile oxide. Osmium is found in platinum ores as an alloy with iridium, known as osmiridium, which is described under iridium (p. 1438). It may be separated from the other members of the platinum group by means of its property of combining directly with oxygen to form a very volatile tetroxide, OsO_4. This compound is obtained, more or less pure, in the course of the preparation of the other platinum metals, and especially of ruthenium (see p. 1389). The solution thus obtained may be precipitated with ammonia and ammonium sulphide, and the precipitated sulphide mixed with sodium chloride, and heated in a slow current of chlorine. The mass when lixiviated yields sodium osmichloride, Na_2OsCl_6, and from this solution ammonium osmichloride is thrown down by ammonium chloride. This is next washed with ammonium chloride solution, and then heated in a covered crucible, when spongy osmium is obtained. The sulphide may also be simply heated in a well-covered carbon crucible to the temperature of the melting point of nickel.

Pure osmium was obtained by Deville and Debray,[2] by passing the vapour of the pure tetroxide mixed with carbon monoxide and carbon dioxide through a red hot porcelain tube. Thus prepared, the metal assumes the form of an amorphous powder, which is converted into the crystalline variety when fused with from three to four times its weight of tin in a charcoal crucible, the crystalline alloy treated with hydrochloric acid, and the residue heated in a current of hydrogen chloride.

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[1] *Phil. Trans.*, 1804, 94, 411.

[2] *Compt. rend.*, 1876, 82, 1076.

The crystalline form of osmium is either that of the cube or of a very obtuse rhombohedron. The crystals possess a bluish-white colour with violet lustre, are harder than glass, and possess a specific gravity of 22·477. Hence osmium is the heaviest of known bodies, and is likewise one of the most infusible and least volatile of the metals. The melting point of the metal is about 2500°; it may be distilled at the highest temperature of the electric furnace, but the volatilisation takes place much more slowly than that of the other platinum metals.[1]

Osmium undergoes oxidation somewhat readily when finely divided, being oxidised and volatilised when heated in air below 212° and in oxygen between 155° and 170°. When strongly heated in air, oxidation of the compact metal also takes place; this operation is dangerous owing to the formation of the highly poisonous tetroxide. Deville was rendered almost blind for twenty-four hours by having accidentally become exposed to the vapour of the tetroxide. This substance produces violent pain and inflammation of the conjunctiva, and vision is permanently injured by reduction to a film of metallic osmium.[2]

In the finely divided state osmium possesses great catalytic activity. It causes oxygen and hydrogen to unite and is a valuable catalyst in the synthesis of ammonia from its elements.[3] Many organic compounds can be oxidised by oxygen in the presence of the metal.[4]

Crystalline osmium is not attacked even by aqua regia, and must be brought into solution by fusion with sodium peroxide, caustic soda and potassium nitrate, or barium peroxide and nitrate; the amorphous metal, on the other hand, is readily dissolved by fuming nitric acid, more slowly by aqua regia.

On account of its high melting point, osmium has been employed for the preparation of filaments of incandescent electric lamps, but the cost is high and tungsten is now more generally employed. The alloy osmiridium, or osrid, which is not attacked by acids, is employed for tipping gold fountain pens, and, inasmuch as it is unoxidisable and non-magnetic, it has been used for compass- and watch-bearings.

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[1] Moissan, *Compt. rend.*, 1906, 142, 189.

[2] *Ann. Chim. Phys.*, 1859, [3], 56, 400.

[3] Haber and Le Rossignol, *Zeit. Elektrochem.*, 1913, 19, 53.

[4] Willstätter and Sonnenfeld, *Ber.*, 1913, 46, 2952.

Colloidal Osmium.—The metal may be obtained in the colloidal condition by reducing potassium osmate with hydrazine hydrate in presence of sodium lysalbate or protalbate[1] or gum arabic,[2] and dialysing the product. This still contains oxygen, which is removed by heating in hydrogen at 30–40°, the residue being completely soluble in water. The colloid may also be obtained by impregnating lanolin with potassium osmate solution and reducing the mass with hydrazine hydrate. This is then dissolved in light petroleum and precipitated by alcohol. The colloidal osmium dioxide thus obtained is reduced by heating in a current of hydrogen at 50° to 60°. The colloidal metal then left is soluble in ether, benzene, or light petroleum, and solutions containing as much as 21 per cent. of osmium may be prepared in this way.[3] It effects the catalytic decomposition of hydrogen peroxide more rapidly than any of the other colloidal metals of this group, and actively decomposes formic acid to carbon monoxide and hydrogen.[4] Carbon monoxide and oxygen combine to form carbon dioxide when shaken with the sol, even at the ordinary temperature.[5] The colloid is more active than the finely divided metal in the oxidation of organic compounds.[6]

COMPOUNDS OF OSMIUM.

OSMIUM AND OXYGEN.

624 The following oxides are known: Osmium monoxide, OsO, osmium sesquioxide, Os_2O_3, osmium dioxide, OsO_2, osmium tetroxide, OsO_4.

In addition to these, osmic acid, H_2OsO_4, and its salts are known, but the corresponding oxide has not been prepared.

The first three of these oxides act as feeble basic oxides, but very few of their salts have as yet been examined, only the sulphite and chloride corresponding to the monoxide, and double chlorides of the formula $3M^ICl,OsCl_3$, corresponding to the sesquioxide, being known. The chloride, $OsCl_4$, has, however, been prepared along with double chlorides corresponding to the derivatives of chloroplatinic acid. Osmic acid forms a series of osmates with the alkali metals, whilst the tetroxide yields a neutral solution in water, and forms salts with neither acids nor bases, though it yields compounds with the alkali hydroxides.

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[1] Paal and Amberger, *Ber.*, 1907, **40**, 1392, 2201.

[2] Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 452.

[3] Amberger, *Kolloid Zeit.*, 1915, **17**, 47.

[4] Muller and Sponsel, *Zeit. Elektrochem.*, 1922, **28**, 307.

[5] Paal, *Ber.*, 1916, **49**, 548.

[6] Willstätter and Sonnenfeld, *Ibid.*, 1914, **47**, 2801.

Osmium Monoxide, OsO, obtained by igniting the corresponding sulphite mixed with sodium carbonate in a current of carbon dioxide, is a greyish-black powder insoluble in acids.

Osmium Sesquioxide, Os_2O_3, is a black powder, insoluble in acids, obtained by heating its salts with sodium carbonate in a current of carbon dioxide. Deville and Debray obtained this oxide in copper-red scales, together with the metal, by the reduction of the tetroxide. A brownish-red *hydroxide* is precipitated by alkalis from solutions of the osmochlorides of the alkali metals.

Osmium Dioxide, OsO_2, is obtained from its salts in a similar way to the foregoing oxides. It is likewise formed when its hydroxide is heated in a current of carbon dioxide. It may also be prepared pure by heating osmium in a current of osmium tetroxide and nitrogen at about 650°.[1] Obtained in this way, it forms masses having a coppery lustre and specific gravity 7·71. On heating, it begins to decompose at about 500° into osmium and osmium tetroxide, but if it is heated in the vapour of the tetroxide the decomposition temperature is 650°. By heating at just below this temperature it is converted into copper-coloured crystals of specific gravity 7·91.[1] When mixed with the combustible substances osmium dioxide deflagrates on heating.

A hydrated osmium dioxide is obtained by hydrolysis of potassium or ammonium osmichloride with caustic potash:

$$K_2OsCl_6 + 4H_2O = OsO_2,2H_2O + 2KCl + 4HCl.$$

The same substance is produced by the action of alcohol or other reducing agents on a solution of the tetroxide or alkali osmate,

$$K_2OsO_4 + 2H_2O + C_2H_5{\cdot}OH = \\ OsO_2,2H_2O + 2KOH + CH_3{\cdot}CHO,$$

or when potassium osmate is exposed to the sunlight or treated with nitric acid. Claus and Jacoby[2] regarded the black precipitate obtained in this way as osmium tetroxide, $Os(OH)_4$, and Moraht and Wischin[1] as osmic acid, H_2OsO_4, *i.e.*, OsO_3,H_2O. Later investigation[2] shows that the substance is the dihydrate of osmium dioxide, $OsO_2,2H_2O$, which loses one molecule of water at 100°, and the other at 200°, leaving the dioxide in a very finely divided and active state. It combines with hydrogen with almost explosive violence and reacts briskly with oxygen to form the tetroxide. When prepared by precipitation with alcohol or from impure ammonium osmichloride, it contains small quantities of organic matter and is then liable to ignite, or, if warm, to detonate on exposure to air.

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[1] Ruff and Rathsburg, *Ber.*, 1917, 50, 484.

[2] *J. pr. Chem.*, 1863, 90, 65.

The dioxide obtained in the above reactions is in the colloidal form and gives a solution which is black by reflected and blue by transmitted light. It is precipitated by electrolytes, but gives a colloidal solution again when washed free from them or when treated with alkali hydroxides or ammonia.[3] A more stable colloid is produced by reducing potassium osmate with hydrazine hydrate in the presence of lanolin as protective colloid.

Osmium Trioxide, OsO_3, is unknown, and the corresponding *osmic acid*, H_2OsO_4, believed by Moraht and Wischin to be produced in the manner just described, is also of doubtful individuality. The corresponding salts, however, are a well defined class of substances known as the *osmates*.

Potassium Osmate, $K_2OsO_4,2H_2O$, is obtained by the addition of alcohol or other reducing agents to the solution of the tetroxide in caustic potash. The liquid becomes of a fine red colour, and, when sufficiently concentrated, the salt separates out as a crystalline powder. When slowly crystallised it forms octahedra which, according to their size, are of a garnet-red or almost black colour. They possess a sweet, astringent taste, and do not change on exposure to dry air, but both in solution and in moist air they decompose, especially on addition of an acid, with formation of tetroxide and lower oxides.

The *sodium* salt crystallises less easily, and yields an aqueous solution having a rose-red colour, from which barium chloride precipitates $BaOsO_4$ as an amorphous, green, flocculent precipitate slowly changing to lustrous, black, prismatic crystals.

Osmium Tetroxide or *Perosmic Anhydride* (commonly called osmic acid), OsO_4.—Very finely divided metallic osmium oxidises slowly at the ordinary temperature, and about 400° takes fire with formation of the above oxide. The denser the metal the higher is the temperature needed for oxidation. Osmium tetroxide may be obtained also by heating the metal in a current of steam, and by dissolving the lower oxides or the metal in nitric acid or aqua regia. These reagents, however, do not attack the metal after it has been strongly ignited. Osmium tetroxide sublimes in transparent, glistening needles which become soft and may be moulded in the hand like wax, and melt at 45°.[1] They begin to sublime at a very moderate heat, and the fused oxide boils at 100°, yielding a colourless vapour with a density of 8·89, which is slightly greater than the calculated value. The crystals dissolve readily in water, forming a colourless liquid which possesses a caustic and burning taste, and does not redden litmus paper. Though it does not give salts, its acidic properties are illustrated by the formation with alkalis of compounds such as $OsO_4,2KOH$, $OsO_4,RbOH$, $OsO_4,CsOH$, and $2OsO_4,CsOH$. These are crystalline bodies, orange or brown in colour. They are soluble in water and are strongly hydrolysed in solution.[2] Osmium tetroxide has a most powerful penetrating smell, somewhat analogous to that of chlorine and iodine. A very small quantity of vapour mixed with air attacks the lungs, giving rise to very serious inflammation of the mucous membrane. As an antidote to the effects of the tetroxide, Claus recommends the inhalation of sulphuretted hydrogen, which, however, must be cautiously employed. Osmium tetroxide also acts violently on the skin, causing a painful eruption which can be removed by the use of sulphur baths. The vapour also acts, as has been stated, most violently on the eyes, and may produce most serious consequences.[3]

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[1] *Zeit. anorg. Chem.*, 1893, 3, 153.

[2] Ruff and Bornemann, *Zeit. anorg. Chem.*, 1910, 65, 429; Ruff and Rathsburg, *loc. cit.*

[3] Ruff and Rathsburg, *loc. cit.*

When heated on red hot charcoal it deflagrates like nitre. It is easily converted into lower oxides by reducing substances, and its alkaline solution when boiled with a salt of formic acid yields a blue precipitate. Sulphur dioxide colours the aqueous solution yellow, then brown, green, and at last indigo-blue.

It is used in microscopic work for staining preparations and also for taking finger prints,[4] the oxide being reduced to metallic osmium.

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[1] Ruff and Tschirch, *Ber.*, 1913, **46**, 929.

[2] Tschugaev, *Compt. rend.*, 1918, **167**, 162.

[3] Deville and Debray, *Ann. Chim. Phys.*, 1859, [3], **56**, 400; *Compt. rend.*, 1874, **78**, 1509.

[4] Mitchell, *Analyst*, 1920, **45**, 125.

Osmium tetroxide acts as a catalyst in many oxidations. Thus, in the presence of a very small quantity of this substance, oxygen will oxidise methyl alcohol to formaldehyde and formic acid, and ethyl alcohol to acetaldehyde and acetic acid.[1] Potassium chlorate which, alone, acts not at all, or only extremely slowly, in the presence of osmium tetroxide readily oxidises arsenic to arsenic acid, hypophosphorous acid to phosphoric acid, potassium formate to carbon dioxide, hydrazine sulphate quantitatively to nitrogen; and a number of organic substances are similarly oxidized.[1] The catalytic action of the tetroxide in these reactions is attributed to the formation of an additive compound with the chlorate. Osmium tetroxide also acts as a catalyst in reductions, and may be employed in the same way as nickel (p. 1368) for the hydrogenation or hardening of oils. The tetroxide is then first reduced to the dioxide[2] and probably the metal.[3]

Osmyl Salts.—When osmium tetroxide is treated with a suitable reducing agent in the presence of certain salts, compounds containing the group OsO_2 are obtained having the general formula $M^I_2(OsO_2)X_4$.[4]

Potassium Osmyl Nitrite, $K_2(OsO_2)(NO_2)_4$, is prepared by reducing the tetroxide with nitric oxide in the presence of potassium nitrite:

$$2KNO_2 + OsO_4 + NO = K_2(OsO_2)(NO_2)_4.$$

The salt crystallises in orange-red prisms but is unstable, readily decomposing into the substances from which it was obtained.

Potassium Osmyl Chloride, $K_2(OsO_2)Cl_4$, is obtained by treating potassium osmate with excess of hydrochloric acid and warming the solution:

$$K_2OsO_4 + 4HCl = K_2(OsO_2)Cl_4 + 2H_2O.$$

On rapidly cooling the solution the anhydrous salt crystallises out as red octahedra, but by slowly cooling the solution the dihydrate may be obtained as pale brown, triclinic crystals. The salt is also obtained by the action of hydrochloric acid on osmyl nitrite.

Many other potassium salts have been similarly prepared, and the corresponding barium and silver salts are obtained by double decomposition.

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[1] Hofmann, *Ber.*, 1913, **46**, 3329; Hofmann, Ehrhart, and Schneider, *ibid.*, 1913, **46**, 1657.

[2] Lehmann, *Arch. Pharm.*, 1913, **251**, 152.

[3] Normann and Schick, *ibid.*, 1914, **252**, 208.

[4] Wintrebert, *Ann. Chim. Phys.*, 1903, [7], **28**, 15.

Osmyl Oxy-salts, having the general formula $M^I_2(OsO_3)X_2$, have also been obtained.[1]

Potassium Osmyl Oxy-nitrite, $K_2(OsO_3)(NO_2)_2$, is prepared by the action of a concentrated solution of potassium nitrite on osmium tetroxide :

$$3KNO_2 + OsO_4 = K_2(OsO_3)(NO_2)_2 + KNO_3.$$

or by the action of potassium hydroxide on the osmyl salt :

$$K_2(OsO_2)(NO_2)_4 + 2KOH = K_2(OsO_3),(NO_2)_2 + 2KNO_2 + H_2O$$

The salt crystallises in nearly black, monoclinic needles.

Ammonium Osmyl Oxychloride, $(NH_4)_2(OsO_3)Cl_2$, is made by the action of hydrochloric acid on the osmyl oxynitrite :

$$(NH_4)_2(OsO_3)(NO_2)_2 + 2HCl = (NH_4)_2(OsO_3)Cl_2 + 2HNO_2.$$

It is a crystalline, yellow powder and with alkaline hydroxides yields the corresponding osmate and ammonia :

$$(NH_4)_2(OsO_3)Cl_2 + 4KOH = K_2OsO_4 + 2KCl + 3H_2O + 2NH_3.$$

OSMIUM AND THE HALOGENS.

625 *Osmium Tetrafluoride*, OsF_4.—By the action of fluorine on finely divided osmium at 250°, the three fluorides are produced. At lower temperatures, or by using a less active specimen of the metal, the product is mainly the tetrafluoride. It has not been isolated in the pure state but its solution in water has been obtained.[2]

Osmium Hexafluoride, OsF_6, is obtained with the two other fluorides by treating the metal with fluorine. The octafluoride is removed (see below) and the hexafluoride obtained by heating at 50° under diminished pressure, when it sublimes and condenses as a light green, crystalline mass. Its boiling point is about 205°. It is decomposed by water, giving osmium oxides and hydrofluoric acid.[3]

Osmium Octafluoride, OsF_8, is obtained as already stated and is formed in greatest amount with an active metal preparation and with a rapid stream of fluorine. It is isolated by evacuating the tubs and collecting in a receiver cooled with liquid air. It is a lemon-yellow, crystalline substance, melting at 34·5° to a

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Wintrebert, *loc. cit.*

[2] Ruff and Tschirch, *Ber.*, 1913, 46, 929.

[3] *Ibid.*, loc cit.

yellowish-red liquid. The vapour is colourless, has a peculiar odour, and vigorously attacks the mucous membrane of the nose and eyes. It begins to decompose at [illegible]25°, the decomposition being appreciable at 400°. Osmium octafluoride violently attacks organic substances. It dissolves in water, and is hydrolysed, the solution having the odour of the tetroxide and not of the octafluoride.[1]

Osmium Dichloride, $OsCl_2$, is obtained in very small amount by heating osmium in chlorine. It is better prepared by heating the trichloride to 500° under reduced pressure and cooling the vapour.[2] It is a brownish-black powder which forms a dark, violet-coloured, unstable solution in water.

Osmium Trichloride, $OsCl_3$, is obtained admixed with the tetrachloride by heating finely divided osmium in chlorine at 1050° and rapidly cooling the vapour. It is prepared in the pure state by heating ammonium osmichloride in chlorine at 350°, when a dark, crystalline sublimate of the trichloride is obtained.[3] It is readily soluble in water.

When osmic acid is boiled for a long time with concentrated hydrochloric acid and a little alcohol, a solution is obtained which on evaporation yields red crystals of the composition $Os_2Cl_7,7H_2O$, which become olive-green in moist air.[4] This appears to be a mixture of the tri- and tetra-chlorides, since, on addition of potassium chloride to the alcoholic solution, potassium osmichloride, K_2OsCl_6, separates, and the filtrate on evaporation yields crystals of the trichloride, $OsCl_3,3H_2O$.

Potassium Osmochloride or *Chlorosmite*, $K_3OsCl_6,3H_2O$, is obtained by adding ammonia to a solution of osmium tetroxide in caustic potash, and saturating the liquid, as soon as it has become yellow, with hydrochloric acid. On evaporation, the above salt separates out together with potassium and ammonium chlorides. The latter can be readily separated mechanically. It forms dark red crystals which effloresce in the air and become pink. It dissolves in water, yielding a cherry-red coloured solution, possessing first a strong astringent and then a sickly sweetish taste.

Ammonium Osmochloride, $2(NH_4)_3OsCl_6,3H_2O$.—In order to prepare this salt, sulphuretted hydrogen is passed into a hydrochloric acid solution of the tetroxide until it has become red.

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[1] Ruff and Tschirch, *loc. cit.*

[2] Ruff and Bornemann, *Zeit. anorg. Chem.*, 1910, **65**, 429.

[3] *Ibid.*, loc. cit.

[4] Moraht and Wischin, *Zeit. anorg. Chem.*, 1893, **3**, 153.

The liquid is then evaporated with sal-ammoniac, when fine, red crystals are deposited resembling the potassium salt.

Osmium Tetrachloride, $OsCl_4$, is obtained by heating the metal in dry chlorine. It forms a red sublimate which dissolves in water, yielding a yellow solution; and this on dilution with more water attains a green tint. On standing, the solution becomes colourless with separation of the lower oxides, whilst hydrochloric acid and osmium tetroxide remain in solution. A solution of osmium tetrachloride is obtained by dissolving the tetroxide in concentrated hydrochloric acid, though with more dilute acids it is reduced to the monoxide or dioxide.[1]

Potassium Osmichloride or *Chlorosmate*, K_2OsCl_6, is obtained by gently heating a mixture of the finely divided metal with potassium chloride in a current of chlorine, and also by evaporating the hydrochloric acid solution of the tetroxide with potassium chloride. It crystallises in dark brown, glistening octahedra, which yield a cinnabar-red powder, and dissolve in water with a yellow colour. Alcohol precipitates the compound from this solution in the form of a red, crystalline powder.

Sodium Osmichloride, $Na_2OsCl_6,2H_2O$, is obtained in a similar way, and crystallises in long, orange-coloured prisms which are easily soluble in water and alcohol.

Ammonium Osmichloride, $(NH_4)_2OsCl_6$, is obtained by the addition of powdered ammonium chloride to a solution of the sodium salt. It is then deposited as a red, crystalline powder, crystallising from dilute solution in brown octahedra.

Another sodium osmium chloride has also been prepared. It has the composition Na_6OsCl_{12}, *i.e.*, $6NaCl,OsCl_6$, and has therefore been called *sodium osmium hexachloride*. It is made by warming sodium sulphonosmate (p. 1434), in a current of hydrochloric acid gas. It forms lustrous, copper-coloured leaflets which cannot be crystallised without decomposition. The *potassium* salt is formed in a similar manner.[2]

Osmium and Bromine.—When osmic acid is boiled with hydrobromic acid and a little alcohol, and the solution evaporated, dark, brown, prismatic crystals of the composition $Os_2Br_9,6H_2O$ are obtained, which are possibly a mixture of $OsBr_3$ and $OsBr_6$. *Osmibromides* have also been prepared.

Osmium and Iodine.—By the action of boiling hydriodic acid on osmic acid, violet-black crystals are formed having a metallic lustre, the composition of which appears to be OsI_4 (Moraht and Wischin). When a solution of potassium iodide, strongly acidified with hydrochloric or phosphoric acid, is added to one of osmium tetroxide, a green substance of the composition $OsI_2,2HI$ is formed. On addition of ether, the latter assumes a green colour even when only traces of osmium are present,[1] and this may be used as a test for the metal. *Osmi-iodides* have also been prepared.

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[1] Remy, *J. pr. Chem.*, 1920, [2], 101, 341; Milbauer, *ibid.*, 1917, [2], 96, 187; Ruff and Mugdan, *ibid.*, 1918, [2], 98, 143.

[2] Rosenheim and Sasserath, *Zeit. anorg. Chem.*, 1899, 21, 122.

Osmium and Sulphur.

626 Metallic osmium burns when heated in sulphur vapour, and sulphuretted hydrogen throws down a dark yellow sulphide of osmium from the hydrochloric acid solution of the oxide. This is slightly soluble in water, giving rise to a dark yellow solution, and easily dissolves in nitric acid.

Osmium Tetrasulphide, OsS_4, is thrown down as a brown precipitate when sulphuretted hydrogen is passed through an aqueous solution of osmium tetroxide. It is insoluble in alkalis and the sulphides of the alkali metals.

Osmium Oxysulphide, $Os_2O_4S_2,H_2O$.—By the action of hydrogen sulphide on the dry dihydrate of osmium dioxide (p. 1427), which they regarded as osmic acid, Moraht and Wischin[2] obtained this compound. The reaction is very violent, much heat being evolved. The oxysulphide is a brown powder which is readily soluble in acids with evolution of hydrogen sulphide. It is possible that water is not present as such in the molecule, and that the formula of the substance is more correctly represented by $Os_2O_3(SH)_2$.

Osmium Sulphite, $OsSO_3$.—In order to prepare this salt, sulphur dioxide is led into an aqueous solution of the peroxide, and sodium sulphate added to the blue liquid. The dark blue gelatinous precipitate, after washing, is dried and yields a powder which is unalterable in the air, and which on trituration exhibits a metallic, silvery lustre. If the blue solution be treated with caustic potash a blackish-blue precipitate of hydroxide is obtained, which on exposure to air absorbs oxygen as rapidly as ferrous hydroxide.

Osmium forms a large number of complex sulphites, which crystallise well and are stable substances. *Sodium osmisulphite*

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[1] Alvarez, *Chem. News*, 1905, **91**, 172.

[2] *Zeit. anorg. Chem.*, 1893, **3**, 153

$Na_8[Os(SO_3)_6],8H_2O$, is obtained by boiling a solution of sodium osmichloride with concentrated sodium hydrogen sulphite, and crystallises in brownish-white prisms. Crystalline compounds have been obtained in which one or more of the SO_3 groups are replaced by the groups Cl or H_2O. The compound $Na_6[Os_4(SO_3)_7],24H_2O$ is obtained as a dull-violet precipitate by the action of sodium hyposulphite on sodium osmichloride.[1]

Complex sulphites of a different series, known as the *sulphonosmates*, are obtained by passing sulphur dioxide through a solution of osmium tetroxide, and then adding an alkali hydrogen sulphite. The *sodium* salt has the composition $3Na_2O,OsO_3,4SO_2,5H_2O$, its constitution being probably $(ONa)_2Os(SO_3Na)_4,5H_2O$. It crystallises in bright brown needles, and is readily soluble in water at 50° to a reddish-brown solution, which soon decomposes to give a black oxide.[2]

OSMIUM AND NITROGEN.

627 Like the other metals of this sub-group, osmium forms complex derivatives with ammonia, but these have not as yet been fully investigated. It also forms complex nitrates, a peculiar acid termed osmiamic acid, $OsNO_3H$, and derivatives containing nitrogen but free from hydrogen and oxygen termed the nitrilo-compounds, which are obtained by the action of acids on the osmiamates.[3]

Osmosammine Hydroxide, $Os[(NH_3)_2(OH)_2]$, is obtained by dissolving the tetroxide in an excess of concentrated ammonia, and heating the reddish-yellow solution in a closed vessel to 50°, when a black precipitate is formed. The flask is then opened and the solution evaporated at a low temperature until the excess of ammonia has been driven off. The base is thus obtained in the form of a blackish-brown powder, which when heated decomposes with rapid evolution of gas. With acids it forms amorphous salts.

Osmyldiammine Chloride, $OsO_2(NH_3)_4Cl_2$, is obtained by the addition of ammonium chloride to a solution of potassium osmate, and forms a yellow, crystalline precipitate easily soluble in water, the solution soon undergoing decomposition.[4]

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[1] Sailer, *Zeit. anorg. Chem.*, 1921, **116**, 209.

[2] Rosenheim and Sasserath, *Zeit. anorg. Chem.*, 1899, **21**, 122; 1900, **24**, 420.

[3] See Werner and Dinklage, *Ber.*, 1906, **39**, 499; Brizard, *Ann. Chim. Phys.*, 1900, [7], **21**, 311.

[4] See also Wolcott Gibbs, *Amer. J. Sci.*, 1873, **3**, 233.

Osmiamic Acid, $OsNO_3H$.—Osmiamates are formed by the action of ammonia on the tetroxide, especially in the presence of potash, the potassium salt being more stable than the ammonium compound. It was at first supposed[1] that this substance had the formula $K_2N_2Os_2O_5$, but Joly[2] has shown that the true formula is $KNOsO_3$, its formation being represented by the equation:

$$OsO_4 + KOH + NH_3 = KNOsO_3 + 2H_2O.$$

The acid has the constitution[3] $\begin{matrix}O\\O\end{matrix}\!\!>\!Os\!<\!\!\begin{matrix}O\\NH\end{matrix}$, the salts being derived from the tautomeric form $\begin{matrix}O\\O\end{matrix}\!\!>\!Os\!<\!\!\begin{matrix}OH\\N\end{matrix}$.

The free acid is obtained by decomposing the barium salt with dilute sulphuric acid, or the silver salt with hydrochloric acid. The light yellow solution remains in the dilute state without change for some time. In the concentrated condition, however, it decomposes to give a gas and a brown powder.

Potassium Osmiamate, $KNOsO_3$, forms orange-yellow tetragonal pyramids, which dissolve slowly in cold, and more readily in hot water, and on crystallisation become dark-coloured, owing to partial decomposition. It decomposes when heated, with loss of nitrogen. Crystalline salts of sodium, barium, and silver are also known.

Osmium Nitrite, $Os(NO_2)_3$, is prepared from barium osminitrite by precipitating the barium exactly with sulphuric acid, and evaporating the resulting solution of osminitrous acid. It forms a deep brown powder.

The double nitrites with the alkali metals and those of the alkaline earths, and of magnesium and zinc, crystallise well, and are soluble in water.[4] *Sodium osminitrite*, $Na_2Os(NO_2)_5,2H_2O$, crystallises in orange-yellow parallelopipeds, and the remaining osminitrites form similar crystals, the colour of which varies from pale to full orange-yellow.

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[1] Fritzsche and Struve, *Petersb. Acad. Bull.*, 1863, **6**, 81.

[2] *Compt. rend.*, 1891, **112**, 1442.

[3] Werner and Dinklage, *Ber.*, 1906, **39**, 499.

[4] Wintrebert, *Compt. rend.*, 1905, **140**, 585.

OSMIUM AND CARBON.

628 Osmium forms a series of osmocyanides, derived from divalent osmium, which correspond closely in composition and in their properties to the ferrocyanides. The most important of these compounds are the following:

Osmocyanic Acid, $H_4[OsCy_6]$, is deposited in the form of white scales on the addition of fuming hydrochloric acid to a solution of the potassium salt. These are easily soluble in alcohol, and crystallise out from the alcoholic solution on the addition of ether in colourless, glistening, transparent, hexagonal prisms. Its aqueous solution has an acid reaction, and from it a substance of the empirical formula $OsCy_2$ separates out as a dark violet precipitate, which, is however, probably a complex osmium osmocyanide.

Potassium Osmocyanide, $K_4[OsCy_6],3H_2O$, is obtained by adding potassium cyanide to an alkaline solution of osmium tetroxide, evaporating the filtered solution, and heating the residue. It crystallises from hot water, in which it is easily soluble, in yellow, tetragonal tablets; these when heated give off water and become colourless. Its solution yields a light blue precipitate with ferrous salts, which becomes darker coloured on exposure to air; when treated with nitric acid, it is converted into a fine, violet-coloured powder, which is also obtained by precipitating the potassium salt with ferric chloride. After drying, this forms a fragile mass having a copper-red colour, and when boiled with caustic potash it yields ferric hydroxide and potassium osmocyanide.

Barium Osmocyanide, $Ba_2[OsCy_6],3H_2O$, is formed when the iron precipitate is boiled with baryta. It crystallises in small, yellowish-red, transparent, rhombic prisms, which are readily soluble in water and alcohol.

Potassium Barium Osmocyanide, $K_2Ba[OsCy_6],3H_2O$, is obtained by mixing hot solutions of the potassium and barium salts. On cooling, small, yellow, oblique rhombohedra are deposited, which are sparingly soluble in cold water.

DETECTION AND ESTIMATION OF OSMIUM.

629 The presence of this metal may be most easily detected by the formation of the volatile strongly-smelling tetroxide. Solutions containing osmium as tetroxide or osmichloride, when

warmed with excess of thiocarbamide and a few drops of hydrochloric acid, give a deep red or rose coloration, and one part in a hundred thousand may be thus detected.[1] Sulphuretted hydrogen throws down a precipitate of the sulphide insoluble in ammonium sulphide. If a solution contain a mixture of the platinum metals, and other metals precipitable by sulphuretted hydrogen, this gas is passed into the hot solution so long as a precipitate is formed. This is then washed and warmed with yellow ammonium sulphide, when platinum, iridium, gold, etc., dissolve. The filtrate is then acidified with hydrochloric acid, the precipitate fused with sodium carbonate and sodium nitrate, and the fused mass lixiviated with water, the residue being treated according to the method described under platinum. In this way the iridium is obtained together with platinum and gold, and these may be readily separated. The portion insoluble in ammonium sulphide is then fused with caustic potash and potassium chlorate, and treated with water in order to dissolve the potassium salts of ruthenic and osmic acids. The solution is carefully neutralised with nitric acid in order to separate the black oxide of ruthenium, and the filtrate distilled with nitric acid, when the volatile osmium tetroxide passes over. The residue insoluble in water is gently ignited in a current of hydrogen, and treated with dilute nitric acid, when palladium and rhodium remain behind, and these are separated by aqua regia, in which the latter metal is insoluble.

Osmium is usually estimated *quantitatively* as the metal. It is separated from other metals as the volatile tetroxide, the vapours of which, in order to avoid loss, are passed into caustic potash; alcohol is added to the distillate in order to form potassium osmate, and the solution then treated with ammonium chloride and the precipitated osmyldiammine chloride ignited in hydrogen, when the metal is obtained.

Osmium tetroxide may also be estimated by adding dilute sulphuric acid and potassium iodide to its aqueous solution, and titrating the liberated iodine. One molecule of osmium tetroxide liberates four atoms of iodine.[2]

The Atomic Weight of osmium was determined by Berzelius in 1828, in a similar way to that of platinum, and he obtained the number 198·9, whilst Frémy,[3] in 1844, by converting the metal into the tetroxide, obtained the number 199·6. According to these determinations, the atomic weight of osmium appeared to be greater than that of iridium, whereas the analogies of the metal with ruthenium seemed to indicate that it should precede iridium in the periodic system, just as ruthenium precedes rhodium. In 1888 Seubert[1] redetermined the atomic weight by analysing pure potassium and ammonium osmichlorides and obtained the number 191·4, whilst in 1891, from a later[2] and more concordant series of experiments, he obtained the still lower number 190·6. The value now (1922) adopted is 190·9.

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[1] Tschugaev, *Compt. rend.*, 1918, **167**, 235.

[2] Klobbie, *Journ. Chem. Soc.*, 1899, **76**, ii, 184.

[3] *Ann. Chim. Phys.*, 1844, [3], **12**, 514.

IRIDIUM. Ir = 193·1. At. No. 77.

630 The history of the discovery of this metal has already been described under osmium.

Iridium is found in the platinum ores in considerable quantity in the form of the alloys platiniridium and osmiridium. The first of these occurs in grains, and often in small cubes with rounded edges; the second usually in flat, irregular grains, and occasionally in hexagonal prisms. The composition of these minerals is shown in the following analyses:

	Platiniridium.		Osmiridium.			
	Urals.	Brazil.	Urals.	New Granada.	California.	Australia.
Iridium	76·85	27·79	55·24	57·80	53·50	58·13
Osmium	—	—	27·23	35·10	43·40	33·46
Platinum	19·64	55·44	10·08	—	—	—
Rhodium	—	6·86	1·51	0·63	2·60	3·04
Ruthenium	—	—	5·85	6·37	0·50	5·22
Palladium	0·89	0·49	trace	—	—	—
Iron	—	4·14	trace	0·10	—	—
Copper	1·78	3·10	trace	0·06	—	0·15
	99·16	97·82	99·91	100·06	100·00	100·00

Iridium is usually prepared from the alloys described above which are left behind when platinum ores are treated with aqua regia. One of the most efficacious of the many methods[1] which have been proposed for the extraction of the metal is that employed by Deville and Debray[2] in the production of the pure iridium required for the standard metre bars of platinum-iridium prepared for the International Commission on the Metric System. The osmiridium is fused with zinc, and heated until all the zinc evaporates, the porous residue being then powdered and ignited with barium nitrate, which converts the iridium into oxide and the osmium into barium osmate. The residue after extraction with water is boiled with nitric acid, which brings the iridium into solution, whilst the osmium is volatilised in the form of tetroxide. The iridium oxide is precipitated from the residual solution by baryta, dissolved in aqua regia, and then thrown down as the double chloride of iridium and ammonium. This, on ignition, yields spongy iridium, containing small quantities of platinum, ruthenium, and a little rhodium. The metal is then ignited with potassium nitrate, and the mass treated with water, when potassium ruthenate dissolves. It is lastly fused with lead, the regulus obtained leaving, after treatment with nitric acid and aqua regia, a residue of pure iridium.

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[1] *Ber.*, 1888, **21**, 1839.

[2] *Annalen*, 1891, **261**, 257.

Another method frequently employed is to mix the "osrid" with sodium chloride and heat to redness in an atmosphere of chlorine. The metals are then converted into chlorides, and the osmium chloride, being volatile, is expelled. The mixed chlorides are then dissolved in water, the solution treated with chlorine and hydrochloric acid and excess of potassium chloride added. A precipitate of the double chlorides of potassium and platinum, iridium, and ruthenium is produced, which is filtered off and boiled with water. Hydrogen is then passed through the solution when platinum and ruthenium are precipitated and the solution becomes green. The solution is decanted from the precipitate and hydrogen again passed through, when the iridium slowly separates out as bright lustrous, thin laminæ.

After osmium, iridium is the most difficultly fusible and least volatile of the platinum metals, but it may be fused and volatilised in the electric furnace; the melting point is 2300°. The molten metal dissolves carbon, which separates out on cooling as graphite. It possesses a white lustre, resembling that of polished steel. In the cold it is very brittle, but at a white heat it is somewhat malleable. The specific gravity of the fused metal is 21·15, whilst that of the crystallised metal is 22·4.

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[1] Wöhler, *Pogg. Ann.*, 1833, **31**, 161; Claus, *Annalen*, 1858, **107**, 134; Gibbs, *Amer. J. Sci.*, 1861, [2], **31**, 70; Matthey, *Proc. Roy. Soc.*, 1879, **28**, 463.

[2] *Compt. rend.*, 1874, **78**, 1502.

If the alcoholic solution of the sulphate be exposed to sunlight the metal is deposited as an impalpable, black powder, which, when washed with hot water and dried, acts even more energetically in bringing about the combination of combustible gases than does platinum black. The smallest trace brought on to paper saturated with alcohol produces ignition, the metal at the same time being converted into a grey sponge.

Spongy iridium is prepared by igniting the double chloride of iridium and ammonium. It absorbs hydrogen, the absorption being a minimum at 0° with falling temperature and a maximum at 20° with rising temperature. The hydrogen is easily expelled by a slight increase in temperature, but the last traces are removed only by strong heating.[1] The spongy metal oxidises when heated in the air, and when ignited becomes dense and lustrous, and then absorbs oxygen only slowly, whilst the coherent metal does not do so at all.

A very active metal is produced when iridium foil is subjected to long-continued cathodic pulverisation in a vacuum, the surface becoming dull and brittle. It absorbs 800 times its own volume of hydrogen at the ordinary temperature. It explodes electrolytic gas and forms an amalgam with mercury which is completely soluble in aqua regia.[2]

Iridium black, as well as the coherent metal when alloyed with much platinum, dissolves in aqua regia. Pure massive iridium is, however, not attacked. When it is heated with acid potassium sulphate, or in presence of fused alkalis, it is oxidised, and it unites directly with chlorine at a dull red heat. When the metal is held in the middle of a flame of alcohol it becomes covered with a black, moss-like deposit, which has the composition IrC_4, and easily takes fire on exposure to the air. The metal is in this case penetrated throughout its mass with carbon, and becomes of a dark grey colour. The oxides also are converted into the carbide of iridium, with evolution of light and heat, when they are heated in gases or vapours containing carbon.

Owing to its brittleness it is very difficult to roll it into foil or draw it out into wire. These difficulties, however, have been overcome, and the metal is employed for the manufacture of scientific apparatus.

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[1] Gutbier, Ottenstein, and Weise, *Ber.*, 1919, **52**, [*B*], 1366.

[2] Rother, *Ber. K. Sachs. Ges. Wiss. Math.-Phys. Kl.*, 1912, **64**, 5.

Iridium is sometimes used for pointing gold pens, and is first heated with phosphorus, which renders it more fusible and easy to work. The phosphorus is afterwards removed by heating the mass in a lime crucible.

It forms an alloy with 9 parts of platinum, which is extremely hard, as elastic as steel, perfectly unalterable in the air, and capable of taking an exceedingly fine polish. This alloy has been employed in the production of standard metre bars and for electrodes to be used in corrosive liquids. A similar alloy is used for the wires of high temperature pyrometers.

Colloidal Iridium may be prepared by sparking between iridium electrodes under cold water (Bredig's method). It is also obtained by the reduction of iridium salts with hydrazine hydrate in presence of sodium protalbate or lysalbate[1] or gum arabic[2] as protective colloids, or by reducing colloidal solutions of the tetrahydroxide with hydrogen, sodium formate, or formaldehyde.[3] The colour of the solution varies from red to black. It possesses considerable catalytic activity. Carbon monoxide and oxygen combine when shaken with the solution at the ordinary temperature.[4] The decomposition of hydrogen peroxide is catalytically accelerated, but not so greatly as by colloidal platinum. The catalyst is "poisoned" by hydrogen sulphide, mercuric chloride, and potassium cyanide.[5]

COMPOUNDS OF IRIDIUM.

631 Iridium forms two basic oxides, the sesquioxide, Ir_2O_3, and the dioxide, IrO_2, and two corresponding series of salts, the sesqui-salts, of the general formula IrR'_3 and the iridic salts IrR^I_4. The halogen compounds form double salts with the corresponding alkali compounds, which must be looked upon as alkali salts of complex acids. Compounds in which the metal is divalent are also known, but have only been slightly investigated. Like the other members of this group, iridium forms numerous complex derivatives, the chief of which are the halogen derivatives just mentioned, the double cyanides, and the ammoniacal derivatives.

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[1] Paal and Amberger, *Ber.*, 1905, **38**, 1398; 1907, **40**, 1392, 2201.

[2] Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 358.

[3] Paal, Biehler, and Steyer, *Ber.*, 1917, **50**, 722.

[4] Paal, *Ber.*, 1916, **49**, 548.

[5] Brossa, *Zeit. physikal. Chem.*, 1909, **66**, 162.

IRIDIUM AND OXYGEN.

632 *Iridium Sesquioxide*, Ir_2O_3, is formed when potassium iridichloride, K_2IrCl_6, is mixed with sodium carbonate and heated to dull redness:

$$2K_2IrCl_6 + 4Na_2CO_3 = Ir_2O_3 + 8NaCl + 4KCl + 4CO_2 + O.$$

The fused mass is washed with water containing ammonium chloride, and the residue, after ignition to expel the ammonium chloride, is treated with dilute acid in order to remove the small quantity of alkali. It is also obtained impure by mixing air-free solutions of potassium hydroxide and sodium iridiochloride, Na_3IrCl_6, evaporating to dryness, and heating the residue to redness in a current of carbon dioxide.[1]

Iridium sesquioxide is a bluish-black powder which is decomposed by heat. At 400°, it is converted into a mixture of the metal and the dioxide, a little oxygen also being lost at this temperature.[1] It evolves oxygen rapidly at 1139°, leaving metallic iridium.[2]

Iridium sesquioxide is readily reduced by hydrogen. In the pure state it imparts to porcelain after firing a fine black colour, and with zinc oxide it yields a grey tint.

Iridium Trihydroxide, $Ir(OH)_3$, is obtained by a process similar to that employed for the preparation of the corresponding rhodium compound (p. 1402), which it closely resembles. It forms a yellowish-green precipitate which readily dissolves in alkalis and oxidises quickly in the air.

Iridium Dioxide, IrO_2, is a black powder obtained by heating the hydroxide in a current of carbon dioxide. It is also formed when the metal is heated to bright redness in the air,[3] or in oxygen, the best temperature for its formation being 1070°. On heating, it decomposes into the metal and oxygen.[4] It is insoluble in acids.

Iridium Tetrahydroxide, $Ir(OH)_4$, is formed by the oxidation of the trihydroxide in the air, or by precipitating the tetrachloride with an alkali, as well as by boiling potassium iridate with ammonium chloride. It is a heavy, indigo-blue powder which is almost insoluble in dilute sulphuric and nitric acids, but dissolves completely, though slowly, in hydrochloric acid. Its solubility, however, appears to depend on the method of preparation.[1] On heating the indigo-blue solution it becomes green and then brown.

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[1] Wöhler and Witzmann, *Zeit. anorg. Chem.*, 1908, 57, 323.

[2] Deville and Debray, *Compt. rend.*, 1878, 87, 441.

[3] Geisenheimer, *Ibid.*, 1890, 110, 855.

[4] Wöhler and Witzmann, *Zeit. Elektrochem.*, 1908, 14, 97.

Iridium tetrahydroxide has also been obtained in the colloidal form. On the addition of potassium hydroxide to potassium iridichloride in the cold, a violet, colloidal solution of the tetrahydroxide is obtained which turns blue on heating.[2] If iridium chloride is added to sodium protalbate or lysalbate, an olive-green or rust-brown precipitate of the protalbate or lysalbate is obtained, the colour depending on the acidity of the solution, and on dissolving this precipitate in sodium hydroxide or carbonate, blood-red hydrosols of iridium trihydrate are obtained, which, in the presence of excess of sodium hydroxide, are oxidised, giving blue hydrosols of the tetrahydroxide.[3]

Potassium Iridate is obtained as a partially soluble bluish mass when iridium is ignited with potassium nitrate. Its composition is not definitely known.

SALTS OF IRIDIUM.

633 *Iridium Monochloride,* IrCl, is obtained by heating the dichloride in chlorine between 773° and 798°. It forms copper-red crystals of specific gravity 10·18. It is insoluble in bases and acids, including even concentrated sulphuric acid.[4]

Iridium Dichloride or *Iridious Chloride,* $IrCl_2$, is formed as a brown, crystalline substance by heating the trichloride in chlorine between 763° and 773°. Above this temperature, it further decomposes into the monochloride.[5] It has been stated to be formed as a green mass when chlorine is passed over spongy iridium at a red heat. Like the monochloride, it is insoluble in bases and acids.

Iridium Trichloride, $IrCl_3$, is best prepared by heating the reduced metal in chlorine at 600°.[6] It is stable in chlorine from below 100° to 763°, when it decomposes into the dichloride, which, in turn, is stable up to 773°, when the monochloride is formed. The trichloride is also obtained by heating one of its double salts with sulphuric acid. If the mass be then thrown into water, the chloride separates out as a light olive-green precipitate containing water and hydrochloric acid, and may be obtained almost anhydrous by heating at 200° to 500° in a current of hydrochloric acid.[1] It may also be prepared by heating ammonium iridichloride in chlorine at 440°.[2] A solution of the trichloride is obtained by treating the hydrochloric acid solution of the tetrahydroxide with sulphur dioxide until it has become green. Iridium trichloride is an olive-green, crystalline substance which is insoluble in acids and bases. It forms complex derivatives with the chlorides of phosphorus and arsenic.[3]

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[1] See also Joly and Leidié, *Compt. rend.*, 1895, **120**, 1341.

[2] Wöhler and Witzmann, *Zeit. Elektrochem.*, 1908, **57**, 323.

[3] Paal, Biehler, and Steyer, *Ber.*, 1917, **50**, 722.

[4] Wöhler and Streicher, *Ber.*, 1913, **46**, 1577.

[5] *Ibid., loc. cit.*

[6] *Ibid., loc. cit.*

Potassium Iridiochloride or *Chloriridite*, $K_3IrCl_6,3H_2O$, is best obtained from the corresponding iridichloride by heating it with sulphuretted hydrogen, and adding potassium chloride to the olive-green solution. It forms very soluble, green, rhombic prisms which effloresce readily. The monohydrate, isomorphous with the corresponding rhodium compound, is obtained by the action of hydrochloric acid on potassium iridium oxalate as greenish-brown crystals.[4] The sodium and ammonium salts are similar compounds of the formulæ $Na_3IrCl_6,12H_2O$ and $(NH_4)_3IrCl_6,H_2O$.

Iridium Tetrachloride or *Iridic Chloride*, $IrCl_4$, is obtained by dissolving the finely divided metal in aqua regia, or by the solution of iridium tetrahydroxide in hydrochloric acid. When the solution is evaporated at a temperature not above 40°, a black mass is obtained which appears red in thin films, and contains a small quantity of trichloride. The tetrachloride is stable only below 100°, and is formed by the action of chlorine on the metal below this temperature, but the reaction is extremely slow, even with liquid chlorine.[5] The hydrochloric acid solution probably contains *iridichloric acid*, H_2IrCl_6, corresponding to the following compounds.

Potassium Iridichloride or *Chloriridate*, K_2IrCl_6, is obtained by the addition of potassium chloride to the above hydrochloric acid solution. On evaporation, small, blackish-red, regular octahedra, isomorphous with the corresponding platinum compounds, are deposited. These are slightly soluble in cold, and more readily in hot water, but do not dissolve in a saturated solution of an alkali chloride or in alcohol.

[1] Delépine, *Compt. rend.*, 1914, **158**, 264.

[2] Antony, *Gazz.*, 1893, **23**, i, 184.

[3] Geisenheimer, *Compt. rend.*, 1890, **110**, 1004, 1336.

[4] Duffour, *Ibid.*, 1912, **155**, 222.

[5] Wöhler and Streicher, *Ber.*, 1913, **46**, 1577.

Sodium Iridichloride, $Na_2IrCl_6,6H_2O$, is readily soluble in water and crystallises in almost black tablets or prisms, which are isomorphous with the corresponding platinum compound.

Ammonium Iridichloride, $(NH_4)_2IrCl_6$, is obtained by precipitating the acid solution of the chloride by ammonium chloride. It is a dark cherry-red powder, consisting of small, blackish-red octahedra, isomorphous with the corresponding platinum compound. It is considerably more soluble than the platinum salt. One hundred parts of water dissolve 0·566 part of the salt at 0°, and 4·381 parts at 100°.[1]

Iridichlorides of metal-complex bases have also been prepared, *e.g.*, $[Co(NH_3)_6]_2$, $[IrCl_6]_3$.[2]

Iridium Tribromide, $IrBr_3,4H_2O$.—When the blue hydroxide is dissolved in hydrobromic acid, a blue liquid is obtained which loses bromine on evaporation and deposits small, light olive-green, six-sided crystals, having the above composition. They dissolve readily in water, but are not soluble in alcohol, and lose their water of crystallisation at 100°. From the mother-liquor of this salt steel-grey needles of iridiobromic acid, $H_3IrBr_6,3H_2O$, are deposited, having a metallic lustre by reflected light. These lose water at 100° and are converted into a brownish-red mass easily soluble in water or alcohol. The solution decomposes carbonates with formation of iridiobromides.

Potassium Iridiobromide, $K_3IrBr_6,3H_2O$, forms long, olive-green, lustrous, efflorescent, four-sided needles, becoming light green and opaque. They dissolve readily in water.

Ammonium Iridiobromide, $2(NH_4)_3IrBr_6,3H_2O$, is obtained by reducing the corresponding iridibromide with sulphur dioxide and neutralising with ammonium carbonate. It crystallises in dark olive-green prisms, and is isomorphous with the corresponding rhodium salt, with which it crystallises in all proportions.

Iridium Tetrabromide, or *Iridic Bromide*, $IrBr_4$.—The blue hydroxide dissolves in hydrobromic acid, giving rise probably to *iridibromic acid*, H_2IrBr_6. This on evaporation with nitric acid leaves a blue, deliquescent, crystalline mass. It forms, with other bromides, well crystallised *iridibromides*, such as K_2IrBr_6, which crystallises in opaque, lustrous, blackish-blue, regular octahedra.

Iridium Tetriodide, or *Iridic Iodide*, IrI_4, is obtained by boiling the hydrochloric acid solution of the chloride with potassium iodide. It forms a black powder, which yields, with the iodide of the alkali metals, well crystallised double compounds possessin a ruby-red colour.

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[1] Archibald and Kern, *Trans. Roy. Soc. Canada*, 1917–18, [3], **11**, 7. See also Rimbach and Korten, *Zeit. anorg. Chem.*, 1907, **52**, 406.

[2] Benrath, Bucher, and Eckstein, *Zeit. anorg. Chem.*, 1922, **121**, 347.

Iridium Monosulphide, IrS.—The metal burns when ignited in sulphur vapour, giving rise to this compound, which resembles galena in its appearance.

Iridium Sesquisulphide, Ir_2S_3, is precipitated when sulphuretted hydrogen is passed into a solution of a salt of iridium sesquioxide. It is a brown powder, somewhat soluble in water, and slightly so in potassium sulphide and nitric acid.

Iridium Ammonium Pentadecasulphide, $(NH_4)_3IrS_{15}$, crystallises in large, brown, tetragonal octahedra.[1]

Iridium Disulphide, IrS_2, is formed when the powdered metal is heated with sulphur and sodium carbonate, and is formed by the action of sulphuretted hydrogen on lithium iridichloride at 4°. It is a brown powder, insoluble in nitric acid, and decomposes at 300° into its elements.[2]

Iridious Sulphite has not been prepared, but several double salts with sodium sulphite, such as $IrSO_3,3Na_2SO_3,10H_2O$ and $IrH_2(SO_3)_2,3Na_2SO_3,4H_2O$, have been described by Seubert,[3] who obtained them during the separation of iridium from rhodium according to Bunsen's method.

Iridium Sesquisulphite, $Ir_2(SO_3)_3,6H_2O$, is obtained when the hydroxide suspended in water is treated for some time with sulphur dioxide. This compound is found in solution whilst a brown, basic salt remains undissolved. The solution is then evaporated, when the normal sulphite separates out in the form of a yellow, crystalline precipitate which is scarcely soluble in water but dissolves readily in dilute acids. It also forms a number of double salts.

Iridium Sesquisulphate, $Ir_2(SO_4)_3,xH_2O$, crystallises out when a solution of the trihydroxide in sulphuric acid is evaporated in absence of air. It combines with the sulphates of the alkali metals, ammonium and thallium, forming a series of alums having the general formula $M^I_2SO_4,Ir_2(SO_4)_3,24H_2O$, which all crystallise in yellow octahedra.[4]

A double salt of the composition $Ir_2(SO_4)_3,3K_2SO_4,2H_2O$ has also been obtained, which separates from boiling aqueous solution, on cooling, in rectangular or hexagonal crystals.[1]

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[1] Hofmann and Höchtlen, *Ber.*, 1904, 37, 245.

[2] Antony, *Gazz.*, 1893, 23, i, 184.

[3] *Ber.*, 1878, 11, 1761. See also Sailer, *Zeit. anorg. Chem.*, 1921, 116, 209.

[4] Marino, *Zeit. anorg. Chem.*, 1904, 42, 213.

Iridic sulphate, $Ir(SO_4)_2$, was obtained by Berzelius as a yellowish-brown, amorphous mass by oxidation of the sulphide with nitric acid. When warmed with sulphuric acid, it undergoes reduction to a green solution of the sesquisulphate.[2]

Iridionitrites.—The simple nitrite of iridium has not been prepared as it readily forms complex nitrites.

Hydrogen Iridionitrite, $H_3[Ir(NO_2)_6].H_2O$, forms light-yellow, readily soluble needles.[3]

Potassium Iridionitrite, $K_3[Ir(NO_2)_6]$, is best prepared by adding potassium nitrite to a solution of iridium sesquisulphate at 70–80°. It is a white powder, readily soluble in boiling water, but almost insoluble in the cold liquid, and in potassium chloride solution. The corresponding *sodium* salt crystallises with $2H_2O$.[4]

A series of salts in which some of the nitrite groups are replaced by chlorine is also known. They are intermediate between the iridichlorides and iridinitrites and are known as the *chlor-nitrites.*

Cyanogen Derivatives of Iridium.—The chief of these are the iridicyanides, which resemble the ferricyanides, and have been investigated by Martius.[5]

Potassium Iridiocyanide, $K_4[Ir^{II}Cy_6]$, is obtained in colourless prisms when potassium ferrocyanide is gently ignited with iridium.

Iridicyanic Acid, $H_3[Ir^{III}Cy_6]$, is obtained by decomposing the barium salt with dilute sulphuric acid. It is very soluble in water or alcohol, less so in ether, and is deposited from solution in crystalline crusts. It possesses an acid reaction and has an unpleasant taste, and from its solutions hydrochloric acid precipitates a green substance which is probably a complex iridium iridicyanide.

Potassium Iridicyanide, $K_3[IrCy_6]$, is obtained by fusing ammonium iridichloride with potassium cyanide, and also by the decomposition of the barium salt with potassium sulphate. It crystallises in colourless, tetragonal prisms, which are easily soluble in water, but insoluble in alcohol. It is a very stable body, unattacked by chlorine or hydrogen chloride.

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[1] Delépine, *Compt. rend.*, 1906, 142, 1525.

[2] Rimbach and Korten, *Zeit. anorg. Chem.*, 1907, 52, 406.

[3] Gibbs, *Ber.*, 1871, 4, 280.

[4] Leidié, *Bull. Soc. chim.*, 1902, [3], 27, 936. See also Miolati, *Atti R. Accad. Lincei*, 1902, [5], 11, ii, 151.

[5] *Annalen*, 1861, 117, 357.

Barium Iridicyanide, $Ba_3[IrCy_6]_2,18H_2O$.—In order to prepare this compound the crude potassium salt is precipitated with copper sulphate, and the precipitate decomposed with baryta water. It forms hard, transparent, probably tetragonal crystals, which effloresce on exposure, are easily soluble in water, and are attacked with difficulty by acids.

AMMONIACAL DERIVATIVES OF IRIDIUM.

634 Iridium forms ammoniacal derivatives corresponding to iridious chloride, $IrCl_2$, and iridic chloride, $IrCl_4$, which are analogous to the corresponding platinum compounds. It forms also an extended series[1] of compounds corresponding to the trichloride, $IrCl_3$, which are similar to the cobaltic, chromic, and rhodic compounds, and are most probably strictly analogous to these in constitution.

1. *Iridious Compounds.—Dichloro-diammine-iridium (Iridio-ammonium Chloride),* $[Cl_2(NH_3)_2Ir]$, is obtained by heating a solution of iridious chloride with an excess of ammonium carbonate and neutralising the solution with dilute hydrochloric acid. It is a yellow, granular body, insoluble in water. The corresponding hydroxide is not known, and of the other salts only the *sulphato-compound,* $[SO_4(NH_3)_2Ir]$, has been prepared. This is obtained by heating the chloride with sulphuric acid, when easily soluble orange-coloured crystals are formed.

Tetrammine-iridium Dichloride (Iridiodiammonium Chloride), $[(NH_3)_4Ir]Cl_2$, is obtained by prolonged boiling of the preceding chloride with excess of ammonia. On cooling, a whitish precipitate separates, and this is decomposed by boiling water with evolution of ammonia. The hydroxide has not been prepared. The *sulphate* crystallises in rhombic prisms, which are easily soluble in hot water and deflagrate on heating.

2. *Iridic Compounds.—Dichloro-tetrammine-iridium Dinitrate (Iridiammonium Chloronitrate),* $[Cl_2(NH_3)_4Ir](NO_3)_2$, is formed when concentrated nitric acid is gradually added to dichloro-diammine-iridium. It dissolves in hot water, and crystallises in lustrous laminæ. If an excess of hydrochloric acid be added to a solution of this compound, the *chloride* is precipitated, crys-

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[1] Palmaer, *Ber.*, 1889, **22**, 15; 1890, **23**, 3810; 1891, **24**, 2090; *Zeit. anorg. Chem.*, 1895, **10**, 320; 1896, **13**, 211.

tallising from boiling water in violet octahedra. Silver nitrate precipitates only the half of the chlorine which it contains. Sulphuric acid converts the nitrate into the *sulphate*, $[Cl_2(NH_3)_4Ir]SO_4$, which crystallises in fine, greenish needles.

3. *Iridium Sesqui-compounds.—Hexammine-iridium trichloride*, $[(NH_3)_6Ir]Cl_3$, prepared by heating the following compound with ammonia at 140°, forms colourless prisms.

Chloro-pentammine-iridium dichloride (*Purpureo-iridium chloride*), $[Cl(NH_3)_5Ir]Cl_2$, is produced by the action of ammonia on ammonium iridiochloride, and forms yellowish-brown, octahedral crystals, or a flesh-coloured, crystalline powder. Silver nitrate precipitates only two-thirds of its chlorine.

A large number of other pentammine-iridium derivatives have been described, as well as aquo-pentammine, tetrammine, and triammine compounds.

DETECTION AND ESTIMATION OF IRIDIUM.

635 Ammonium chloride produces, in a tolerably concentrated solution of iridium, a dark-red, crystalline precipitate, and the dark colour sometimes observed in the corresponding platinum precipitate indicates the presence of iridium in this metal. Iridium is also distinguished from platinum by the formation of a colourless solution of potassium iridichloride when caustic potash is added to the chloride of the metal; on exposure to the air, this solution first becomes red-coloured, and afterwards blue. Sulphuretted hydrogen decolorises the solution of an iridic salt with separation of sulphur, whilst the brown sulphide, soluble in ammonium sulphide, is precipitated.

Iridium is always estimated quantitatively as the metal.

The Atomic Weight of iridium was determined by Berzelius by igniting potassium iridichloride in hydrogen, the result of a single experiment being 196·5. Seubert,[1] in 1878, working with carefully purified material, obtained the number 192·05 by the analysis of the same salt, whilst the ignition of the ammonium salt gave the higher number 193·39. Joly,[2] in 1890, by the analysis of the potassium and ammonium iridichlorides, obtained the number 193·18. Archibald,[3] in 1909, by reduction of potassium iridichloride in hydrogen, obtained the value 192·90, but no details of the work have yet been published. Hoyermann,[4] in 1911, by reducing ammonium iridichloride in hydrogen obtained, as a mean of five determinations, the value 192·61 and Holzmann,[1] in 1912, adopting the same method, found as a result of four determinations the value 193·42.

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[1] *Ber.*, 1878, **11**, 1770.

[2] *Compt. rend.*, 1890, **110**, 1131.

[3] *Chem. News*, 1909, **100**, 150.

[4] *Sitzungsber. phys. med. Soz. Erlangen*, 1911, **42**, 278.

The number now (1922) adopted is 193·1.

PLATINUM. Pt = 195·2. At. No. 78.

636 This metal appears to have been first observed in the sixteenth century; for Scaliger, who died in 1558, in his work *Exercitationes Exotericæ de Subtilitate*, combated the views of Cardanus that all metals are fusible; for, he adds, in the mines of Mexico and Carian a metallic substance is found "quod nullo igni, nullis Hispanicis artibus, hactenus liquescere potuit." As platinum occurs in the above districts, it appears very probable that this was the metal here referred to. Indeed the metal seems to have been used long before this date, for an alloy containing platinum together with gold and iridium has been found composing some of the hieroglyphs on an Egyptian box discovered at Thebes, dating from the seventh century B.C.[2]

It was not, however, until the eighteenth century that platinum attracted general attention, and this time many chemists occupied themselves diligently with the subject. The first of these was Don Antonio de Ulloa, who took part in the French Expedition of 1735 which had for its object the measurement of an arc of the meridian on the equator. In 1748 he published his *Relacion Historica del Viage a la America Meridional*, in which he describes an unworkable metallic mineral which even makes gold ore useless if it occur mixed with it in large quantities. William Brownrigg[3] was the first to describe native platinum as a compact metal. He had obtained it nine years previously from Charles Wood, who had brought some samples of it from Carthagena in Granada to Jamaica, and thence to England. Brownrigg termed it a semi-metal. It was afterwards more exactly examined by Scheffer, who described it in the Memoirs of the Stockholm Academy in 1752 with the title "On White gold, or the seventh Metal, termed in Spanish 'platina del Pinto,'" that is, small silver of Pinto, *platina* being the diminutive of *plata*, the Spanish for silver. The name of del Pinto was added because it was first found in the auriferous sand of that river. Scheffer describes the insolubility of platinum in nitric acid, and was acquainted with the facts that aqua regia dissolves it and that it is precipitated from the solution by mercury. He also states that it is infusible at the strongest heat of a furnace, but that it can be alloyed with other metals, and that it may be fused by the help of arsenic. He declares the new body to be a true metal, and, on account of its unalterability, believes it to be a noble one, and suggests that it may be used for the specula of telescopes. In 1754 Lewis[1] published a series of researches on platinum, and in 1757 the investigations of Marggraf were communicated to the Berlin Academy. Amongst the most important of his observations was that which has since proved of such service to analytical chemistry, that platinum solution produces with the salts of the alkalis an orange-yellow precipitate, with the exception of that of the mineral alkali soda, with which it produces none. Next came Macquer and Beaumé's researches on platinum, which were published in the Memoirs of the Paris Academy of 1758. The most important new fact observed by these chemists was that platinum can be fused in the focus of a powerful burning-glass. Besides this, the paper in question contains the information that platinum had hitherto been so rare a substance, because the Spanish Government had forbidden its exportation, inasmuch as gold could be alloyed with a considerable quantity of the new metal without its colour being sensibly changed, thus giving rise to the possibility of fraud. Further investigations were made by Cronstedt in 1764, and by Bergman in 1777, the latter chemist explaining the nature of the changes which occur when a platinum solution is treated with the alkalis. Count von Sickingen, at that time the representative of the Palatinate at the Court of Paris, worked diligently on the subject of platinum, and was the first, in 1772, to prepare platinum foil and platinum wire, and to show that this metal when alloyed with silver dissolves in nitric acid. His experiments were communicated to the Academy in 1778, and in 1782 the same researches were described in a pamphlet which appeared in German with the title *Experiments on Platinum*. All the preceding researches, as well as many later ones, were made with South American platinum.

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[1] *Sitzungsber. phys. med. Soz. Erlangen*, 1912, **44**, 84.

[2] Berthelot, *Compt. rend.*, 1901, **132**, 729; *Ann. Chim. Phys.*, 1901, [7], **23**, 5.

[3] *Phil. Trans.*, 1750, **46**, 584.

In 1819 grains of a white metal were discovered in the auriferous sands of the Urals, but it was not till 1823 that platinum was detected in this substance. This discovery gave rise to the Scientific Expedition to the Urals undertaken by Humboldt, G. Rose, and Ehrenburg, in 1829.

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[1] *Phil. Trans.*, 1754, 48, 638.

With the exception of *sperrylite*, $PtAs_2$, found in small quantities in the nickel-copper ores of Ontario,[1] platinum occurs in the native state, but native platinum is very seldom pure, the purest specimens having been found in Brazil together with grains of palladium. The usual platinum "ore," as it is termed, contains all the metals of this group together with iron, copper, titanic iron ore, etc. It is sometimes, though seldom, found crystallised in cubes and octahedra, but more usually occurs in rounded or flattened grains, or sand having a metallic lustre, and occasionally in large, rounded nuggets, both forms occurring in river sand or detritus. Some of the more important localities from which platinum is obtained are Choco near Popayan, the gold-washings of the Pinto in the province of Antioquia in Columbia, and Minas Geraes in Brazil. In the Urals it is found in alluvial deposits at Nischnetagilsk and Goroblagodat. Platinum likewise occurs in the Natoos Mountains in Borneo, and in Haiti, Peru, California, India, and Australia, especially in New South Wales. It is also found in small quantities in the sands of various rivers, occurring in the Rhine, and in streams in Wicklow, North Carolina, and Canada East. The largest mass which has yet been obtained is that in the Demidoff Cabinet in St. Petersburg, weighing 7·837 kilos. In the Urals platinum is found together with chrome iron ore in serpentine, whilst in the Brazils it occurs with gold in syenite. Many common minerals, such as dolomite, heavy spar, and fahl ore, contain traces of platinum, and this explains the occurrence of the metal in the sands of so many rivers. It is found in small quantities also in most of the ores of lead and silver, and it is usually contained with palladium in small quantities in all silver; and it has been observed in meteoric iron.[2] Some American copper ores contain platinum, and it is recovered in the electrolytic refining of copper. In the United States mints the gold is refined electrolytically, and sometimes the anode sludge contains small quantities of platinum. Thus, in the San Francisco mint, 112 ounces of platinum and iridium were recovered from the refining of 1,073,000 standard ounces of gold.

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[1] Walker, *Zeit. Kryst. Min.*, 1896, **25**, 561; *Amer. J. Sci.*, 1896, [4], **1**, 110; Wells and Penfield, *ibid.*, 1902, [4], **13**, 95; Dickson, *ibid.*, 1903, [4], **15**, 137.

[2] Davison, *Amer. J. Sci.*, 1899, [4], **7**, 4.

The following table contains a series of analyses of various platinum ores by Deville and Debray:[1]

Locality.	Choco (S. America).	California.	Australia.	Urals.
Platinum	86·20	85·50	61·40	76·40
Gold	1·00	0·80	1·20	0·40
Iron	7·80	6·75	4·55	11·70
Iridium	0·85	1·05	1·10	4·30
Rhodium	1·40	1·00	1·85	0·30
Palladium	0·50	0·60	1·80	1·40
Copper	0·60	1·40	1·10	4·10
Osmiridium	0·95	1·10	26·00	0·50
Sand	0·95	2·95	1·20	1·40
	100·25	101·15	100·20	100·50

The body termed osmiridium is an alloy of osmium and iridium which is not attacked by aqua regia; the sand contains quartz, chrome iron ore, hyacinth, spinel, and ilmenite.

637 *The Metallurgy of Platinum.*—The infusibility of platinum, as well as its power of withstanding the action of many of the most powerful reagents, rendered it desirable that this metal should be employed for the manufacture of vessels for chemical use. In 1784 Achard mentioned that the substance obtained by fusing arsenic and platinum together leaves, on ignition, a residue of malleable platinum; in this way he prepared what was probably the first platinum crucible. From the year 1787 this method was employed in Paris, where Janetty was celebrated for his platinum work. Platinum vessels were, however, so expensive and difficult to obtain, that in the year 1801 G. Rose and Karsten, for want of a platinum crucible, were unable to examine the statement of Guyton de Morveau and Desormes that potash consists of lime and hydrogen, and soda of magnesia and hydrogen.

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[1] *Ann. Chim. Phys.*, 1859, [3], **56**, 449. See also Martin, *16th Ann. Rept. U.S. Geol. Survey for* 1894–5, Pt. III., 1895, 628; Koifman, *Arch. Sci. phys. nat.*, 1915, [4], **40**, 22.

In the year 1800 Richard Knight[1] published a method for preparing malleable platinum. This consisted in dissolving the crude platinum, precipitating the solution with ammonium chloride, stamping the dried precipitate of the double chloride of platinum and ammonium into a conical mould made of fire clay, and igniting the whole. In this way platinum is obtained as a coherent metallic mass, which can then be worked up. In 1822 a similar method was described by Barrual; but for many years before this, in fact from 1800 to 1809, a relative of a member of the well-known firm of Messrs. Johnson, Matthey and Co. was employed in working on platinum, and had discovered (whether independently of Knight is uncertain) a method for consolidating the sponge, which was afterwards elaborated by Wollaston and described by him in the Bakerian Lecture[2] for 1828. This, although identical in the main features with Knight's process, is distinguished from it in several important particulars, and is the method by which platinum was manufactured up to the year 1859, when Deville's process came into use.[3] Wollaston in the first place pointed out the necessity of heating the double chloride very gently at a temperature just sufficient to expel the whole of the ammonium chloride and to occasion the particles of platinum to cohere as little as possible, for on this depends the ultimate ductility of the product. The metallic powder thus obtained must be rubbed between the hands of the operator so fine as to pass through a fine lawn sieve. After having been well levigated, the uniform mud or pulp is pressed whilst cold into a brass barrel and strongly compressed by a powerful lever. The cake of platinum can be easily removed, owing to the conical form of the barrel, and is so hard that it can be handled without danger of breaking. It is then placed on a charcoal fire and heated to redness to drive off moisture and to give it a greater degree of cohesion. After this it is heated in a wind furnace to the most intense heat that can be obtained. After ignition for about twenty minutes, the cake is removed from the furnace and placed upright on an anvil, and struck when hot with a heavy hammer. The ingot of platinum thus obtained may be drawn into wire or submitted to any of the processes of which the most ductile metals are capable.

The easy method thus proposed for working up platinum has had a great influence on the progress of chemistry. The present generation of chemists can scarcely understand the difficulties with which their predecessors had to contend, unable, as they were, to use platinum crucibles, basins, retorts, foil, or wire. In his *Letters on Chemistry* Liebig says:

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[1] *Tilloch's Phil. Mag.*, 1803, **16**, 1.

[2] *Phil. Trans.*, 1829, **119**, 1.

[3] *Ann. Chim. Phys.*, 1859, [3], **56**, 484.

"Without platinum it would be impossible, in many cases, to make the analysis of a mineral. The mineral must be dissolved and it must be first rendered soluble, or prepared for solution. Now, vessels of glass, of porcelain, and of all non-metallic substances are destroyed by the means we employ for that purpose. Crucibles of gold and silver would melt at high temperatures. But platinum is cheaper than gold, harder and more durable than silver, infusible at all temperatures of our furnaces, and is left intact by acids and alkali carbonates. Platinum unites all the valuable properties of gold and of porcelain, resisting the action of heat, and of almost all chemical agents. Without platinum the composition of most minerals would have yet remained unknown."

Platinum apparatus is also employed on a large scale and with great advantage in the chemical industries; thus, for example, in the manufacture of sulphuric acid, and in the parting of the noble metals. The first platinum apparatus for concentrating sulphuric acid, weighing 423 ounces, was made in London in 1809 by Messrs. Johnson, Matthey and Co., who since that time have furnished platinum vessels for all parts of the world. The price charged for this first platinum still was at the rate of 16*s.* per ounce; the present price is about £20.

The application of the oxy-hydrogen blowpipe for fusing large masses of platinum, proposed first by Hare,[1] has exerted a great influence on the progress of the platinum industry. Hare succeeded in fusing 971 grams of platinum, as well as large quantities of iridium and osmium. This method was improved upon by Deville and Debray,[2] whose investigations on the platinum metals have been of great service to the general progress of chemical industry. The means employed by these chemists for fusing platinum, and now employed on the large scale by most of the platinum manufacturers, consists in the use of two well-fitting lumps of quick lime. The upper one has a hole drilled through the middle for the introduction of the blowpipe, whilst a side opening permits the escape of the products of combustion and serves as an outlet for the molten metal. Instead of hydrogen, common coal-gas is usually employed. This is allowed to enter through the tube H, Fig. 202, whilst the oxygen enters at O. The upper portion of the blowpipe consists of copper and the lower of platinum. Lime is used for the crucible, because it stands a high temperature well, and at the same time it absorbs the slags of the oxides of iron and silicon and other materials which are formed during the operation. The introduction of this process induced chemists to seek for a cheap method of preparing oxygen on the large scale, whilst by means of the oxy-hydrogen blowpipe Messrs. Johnson, Matthey and Co. have succeeded in effecting a most important improvement in the metallurgy of platinum, viz., that of soldering platinum by itself (autogenous soldering), instead, as was formerly the case, of soldering with gold. The electric furnace is now frequently employed for fusing platinum.

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[1] *Phil. Mag.*, 1847, [3], 31, 356.

[2] *Ann. Chim. Phys.*, 1859, [3], 56, 385.

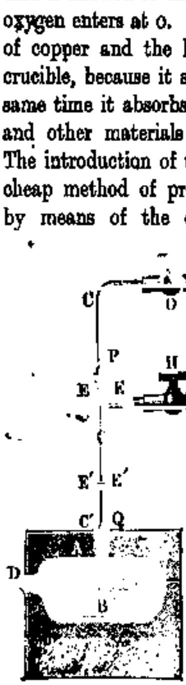

Fig. 202.

Most of the platinum of commerce has been obtained from the Urals by a process of concentration by washing, similar to the manner in which alluvial gold is extracted. The crude platinum thus obtained is in the form of fine particles, grains, and scales; nuggets are also occasionally met with, and a little gold is also generally present. This gold is extracted from the crude platinum by amalgamation, the material being rubbed with mercury in a dish made of wood, iron, or porcelain.

Deville and Debray elaborated two methods[1] for treating in the dry way the crude platinum remaining. According to the first of these, the ore is repeatedly melted in a vessel made of lime. In this way an alloy of platinum with iridium and rhodium is obtained. This method is especially applicable to the fusion of old platinum vessels, inasmuch as all the impurities, such as sulphur, phosphorus, iron, gold, lead, etc., which occur in the scrap platinum, are either volatilised or absorbed by the lime. The second method depends on the fact that lead can be alloyed with the platinum metals but not with osmiridium. These processes have, however, not met with much success in practice, as the platinum thus prepared may contain, besides the harmless iridium and rhodium, other admixtures, and may not be homogeneous.

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[1] *Ann. Chim. Phys.*, 1859, [3], 56, 385; 1861, 61, 5.

Hence wet methods are more generally used. The following process is adopted in the German works of Heräus in Hanau.[1] The raw ore is treated in glass retorts under a pressure of twelve inches of water with a mixture of 1 part of aqua regia and 2 parts of water. The solution is evaporated to dryness, and the dried mass heated to 125°, at which temperature the palladium and rhodium salts are reduced to lower chlorides. The clear aqueous extract acidified by hydrochloric acid is then precipitated with ammonium chloride, the double chloride of platinum and ammonium being thrown down, whilst the corresponding iridium salt is obtained on evaporating the mother-liquor. The solution remaining after precipitating the platinum is treated with scrap iron, when the other metals are thrown down, and the precipitate, from which the excess of iron has been dissolved by hydrochloric acid, is again treated with aqua regia, and from this solution a new portion of platinum and iridium thrown down. The mother-liquors, as well as the residue left on dissolving the ore in aqua regia, contain palladium, rhodium, ruthenium, osmium, and iridium. The spongy platinum obtained by igniting the double chloride of platinum and ammonium is then pressed, broken up, and fused with excess of oxygen in a lime crucible.

In the wet process of G. Matthey the platinum is first melted with six times its weight of lead, and then granulated by pouring into water.

The process employed in Russia is very similar to the foregoing. The crude platinum is dissolved in aqua regia in porcelain basins set on a sand-bath. The solution is repeatedly evaporated with hydrochloric acid until all nitric acid has been removed, the aqueous solution then filtered, and the filtrate treated as described above.[2]

Most of the platinum which occurs in commerce is not pure, but contains, like Russian platinum coin, 2 per cent. of iridium. This alloy is valuable for the preparation of chemical vessels, as it is less readily attacked by acids than pure platinum.

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[1] Philipp, *Ber. Entw. Chem. Ind.*, **1**, 999.

[2] *Mineral Industry*, 1897, **6**, 561.

638 *Preparation of Pure Platinum.*—Deville and Debray[1] have prepared pure platinum on a large scale by the following process. The metal, which contains iridium and rhodium, is fused with six to ten times its weight of lead, the mass after cooling treated with nitric acid, and the residue treated with dilute aqua regia, when a crystalline alloy of iridium, ruthenium, and iron remains behind, whilst lead, platinum, and some rhodium go into solution. This latter is treated with ammonium chloride, the double chloride, $(NH_4)_2PtCl_6$, being thrown down in a finely divided, amorphous state and almost white, whilst the rhodium is kept in solution. The precipitate is washed with water containing hydrochloric acid, ignited, and the residue of platinum fused in a lime crucible. When fused, the supply of gas is suddenly stopped, so that the metal solidifies from the outside; in this way the formation of bubbles in the metal is avoided.

According to G. Matthey,[2] the preparation of pure platinum is a matter of great difficulty. His process is, to begin with, similar to that already described, but he evaporates down the aqua regia solution, and then adds pure sulphuric acid to the residue in order to convert any lead which may remain in solution into the insoluble sulphate. The platinichloric acid is then dissolved out with water and precipitated by a mixture of ammonium chloride and common salt, the latter being added because the ammonium platinichloride is less soluble in a solution of common salt than in water. The liquid is then heated to 80° and allowed to stand for some days in order that the precipitate may become denser. This is then repeatedly washed with a solution of ammonium chloride, and at last with distilled water acidified with hydrochloric acid. The washed precipitate is then dried and mixed with potassium bisulphate and a small quantity of ammonium bisulphate. The mixture is then heated to dark redness in a platinum basin. On boiling the mass with water, potassium sulphate and potassium rhodosulphate dissolve, leaving pure platinum behind.

The production of platinum from the Ural mines, has been subject to great variations. In 1825, when the mines were first opened, only 361 pounds were produced. In 1827 the experiment of coining with platinum was tried at the St. Petersburg mint, pieces of 3, 6, and 12 roubles being produced. The coinage of platinum was, however, soon abandoned (in 1844), and the coins in circulation were withdrawn, owing to the very considerable variations which the price of the metal underwent from year to year and the impossibility therefore of fixing a permanent monetary value upon the coin. The total value coined amounted to 4,146,504 roubles, and the annual amount produced towards the close of the period in which the metal was coined reached 7,716·4 pounds. It afterwards declined, but subsequently increased owing to the large demand for the metal occasioned by the widespread introduction of electric lighting, the metal being employed in the construction of incandescent lamps. In 1893 the production reached the amount of 11,196 pounds.

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[1] *Compt. rend.*, 1875, 81, 893.

[2] *Proc. Roy. Soc.*, 1879, 28, 463.

Later the supply of platinum has not been equal to the increase in demand; Russia is still the chief source of the metal, and the scarcity is partly due to the local difficulty of securing the necessary mining labour, and also to the diminution of yield in the richer mines. The average output of the Russian mines was, for the years 1893 to 1898, 12,050 lb. per annum; for the years 1899 to 1904, 12,600 lb., whilst during the year 1905, 14,050 lb. were produced. There is, however, a small production of platinum in the United States, between 100 and 200 troy ounces being produced per annum; Columbia also produced 800 lb. during 1904, and since that time the output has considerably increased.

639 *Properties.*—Pure platinum has a tin-white colour, is soft like copper, has a specific gravity of 21·4136–21·4317 (Kahlbaum),[1] and is the most malleable of metals after gold and silver. The specific heat of platinum is 0·03159, and this increases with temperature even at very high temperatures.[2] Its coefficient of expansion is very nearly the same as that of glass, so that a platinum-glass join may be made without the latter cracking. Like iron, it can be readily welded at a white heat. It melts at 1710° as determined by a resistance thermometer,[3] whereas higher temperatures, 1753–1889°, are indicated by the optical pyrometer method.[4] An extremely fine wire can be melted in the flame of a Bunsen burner; platinum in large masses is infusible even at the highest temperature of a blast-furnace, although a small piece of the metal may be melted

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[1] *J. Chim. Phys.*, 1904, 2, 337.

[2] Magnus, *Ann. Phys.*, 1916, [4], 48, 983; Fabaro, *Nuovo Chim.*, 1915, [6], 9, i, 123.

[3] Harker, *Proc. Roy. Soc.*, 1906, 76, [*A*], 235.

[4] Waidner and Burgess, *Bull. U.S. Bureau Standards*, 1907, 3, 163; Holborn and Valentiner, *Ann. Physik*, 1907, 22, 1.

in such a furnace.[1] It can, however, be fused in the oxy-hydrogen flame. When large masses of the molten metal are quickly cooled they exhibit the phenomenon of "spitting" so characteristic of silver.

Platinum is sensibly volatile below its melting point, even at 1300°,[2] and cubic or octahedral crystals of the metal have been found in the neighbourhood of the platinum electrodes in electric furnaces.[3] According to Hulett and Berger[4] it begins to volatilise at 800° in air, whilst it is unchanged at this temperature in the absence of oxygen; this phenomenon has been attributed to the formation at high temperatures of a volatile oxide which undergoes decomposition at lower temperatures. Roberts[5] found that platinum does not volatilise in hydrogen, nitrogen, or in vacuo, but begins to do so in oxygen even at 500°, the extent of the volatilisation being nearly proportional to the pressure of the oxygen, and he concludes that the volatilisation is due to the formation of the oxide PtO_2 which decomposes at lower temperatures.

The loss of weight of platinum by heating is increased by the presence of iridium and decreased by rhodium, these effects being particularly noticeable above 900°. Iridium is frequently alloyed with platinum in order to stiffen it for the manufacture of crucibles, but rhodium would be preferable for this purpose. The presence of iron reduces the loss of weight on heating, and below 900° there may even be a gain in weight owing to the iron diffusing to the surface and oxidising.[6] Platinum can be distilled in the electric furnace.[7]

Hydrogen diffuses through platinum,[8] and tubes made from fused and hammered platinum allow hydrogen to pass through them at a strong red heat in larger quantity than is the case with caoutchouc membranes at the ordinary temperature. This property depends upon the fact that the red-hot metal has the power of absorbing hydrogen (Vol. I., p. 159). It dissolves 3·8 volumes of the gas, which it gives off on heating in a vacuum, the surface of the platinum becoming covered with bubbles.[1] The solubility is proportional to the square root of the pressure of the hydrogen and is less than in the case of iron and nickel.[2] The power of platinum to absorb hydrogen is diminished by the presence of mercury, sulphur, arsenic, and zinc, and the extent of the "poisoning" is proportional to the amount of poison present.[3] Such substances also cause a diminution in the catalytic activity of the metal, the extent of the poisoning being different for different reactions.[4] The absorption of hydrogen is also noticed when platinum foil is employed as the negative pole in the electrolysis of water, the hydrogen being given off again when it is converted into the positive pole. Platinum does not dissolve carbon dioxide or sulphur dioxide.[1]

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[1] Meyer, *Ber.*, 1896, **29**, 850.

[2] Crookes, *Proc. Roy. Soc.*, 1912, **86**, 464.

[3] Guntz and Bassett, *Bull. Soc. chim.*, 1906, [3], **35**, 1306.

[4] *J. Amer. Chem. Soc.*, 1904, **26**, 1512.

[5] *Phil. Mag.*, 1913, **25**, 270.

[6] Burgess and Sale, *J. Ind. Eng. Chem.*, 1914, **6**, 452; 1915, **7**, 516; Burgess and Waltenberg, *ibid.*, 1916, **8**, 487.

[7] Moissan, *Compt. rend.*, 1906, **142**, 189.

[8] See Schmidt and Lücke, *Zeit. physikal. Chem.*, 1921, **8**, 152.

In January, 1817, Sir Humphry Davy communicated the fact to the Royal Society that mixtures of oxygen or air with hydrogen, carbon monoxide, ethylene, vapour of alcohol, vapour of ether, and other easily inflammable gases or vapours, are capable of bringing about the incandescence of a warmed platinum wire,[5] and that then these mixtures either combine slowly or in some cases quickly, and even with explosion. This now well-known phenomenon is thus described by Davy: "A temperature much below ignition only was necessary for producing the curious phenomenon, and the wire was repeatedly taken out and cooled in the atmosphere till it ceased to be visibly red, and yet when admitted again it instantly became red hot." In the following year Erman observed that it was only necessary to warm the platinum wire to 50° to enable it to bring about this combination.

In 1820 Edmund Davy showed that the black powder deposited when a platinum solution is precipitated by sulphuretted hydrogen, the precipitate dissolved in nitric acid, and the liquid thus obtained mixed with its own volume of alcohol, possesses the property, when moistened with spirits of wine, of becoming ignited in the air. Two years later, Döbereiner observed that spongy platinum, obtained by the ignition of the double chloride of platinum and ammonium, exhibits the same phenomenon when gently warmed with alcohol. In 1823 the same chemist noticed that when hydrogen is allowed to pass over spongy platinum in presence of air the hydrogen gas is ignited, and upon this was founded the well-known Döbereiner's Hydrogen Lamp.[1] Faraday afterwards showed that chemically clean platinum acts in a similar way. The circumstances in which platinum and certain other metals exhibit this action were investigated by Thénard and Dulong in the same year.

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[1] See also Winkelmann, *Ann. Physik*, 1901, [4], **6**, 104; 1902, [4], **8**, 388; 1906, [4], **19**, 1046; Langmuir, *J. Amer. Chem. Soc.*, 1918, **40**, 1361.

[2] Sieverts and Jurisch, *Ber.*, 1912, **45**, 221.

[3] Maxted, *Journ. Chem. Soc.*, 1921, **119**, 225. Compare Paal and Windisch, *Ber.*, 1913, **46**, 4010.

[4] See Vavon and Husson, *Compt. rend.*, 1922, **175**, 277.

[5] *Phil. Trans.*, 1817, **107**, 77.

In order to exhibit this action, Davy's glow-lamp is used (Fig. 203). It is fed with a mixture of alcohol and ether, or with methyl alcohol; this is ignited in order to heat the spiral of platinum wire to redness. The flame is then blown out, and the mixed vapours of alcohol and ether rising from the moist wick are oxidised, and thus the spiral is kept brightly incandescent. The same phenomenon can be observed if a spiral of platinum wire be hung in a small test-glass (Fig. 204) into which a little ether has been poured. Another mode of showing the same experiment is to heat a small piece of platinum foil in the flame of a Bunsen burner, and then quickly to extinguish the flame, allowing the gas to escape. The foil soon begins to glow, and if it be placed near the burner it becomes hot enough to re-ignite the gas; if further removed, the foil continues to glow, but the gas is not ignited.

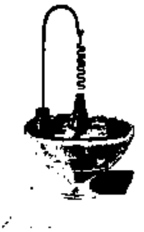
FIG. 203.

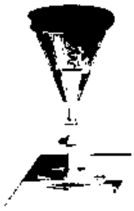
FIG. 204.

The catalytic action of platinum in the oxidation of hydrogen and of carbon monoxide has been studied by Langmuir.[2]

Spongy Platinum, first prepared by E. Davy, is very finely divided metallic platinum, which possesses a very large surface compared with its mass, and is able to condense large quantities of oxygen. This substance is frequently employed as an oxidising agent, and may be readily prepared by gently heating the double chloride of platinum and ammonium. By the action of sodium hydroxide solution on chloroplatinic acid mixed with formaldehyde, a more active product is obtained which becomes incandescent on exposure to air owing to the absorption of oxygen.[1] Spongy platinum forms a porous mass which, when heated strongly, becomes denser, and assumes a metallic lustre under the burnisher.

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[1] *Schweigger's J.*, 42, 60; *Tilloch's Phil. Mag.*, 1825, 66, 160.

[2] *Trans. Faraday Soc.*, 1922, 17, 607.

Platinum Black.—This form of platinum was also discovered by E. Davy, who, however, misled by certain accidental impurities, considered it to be a platinous nitrite. It is to Liebig[2] that we owe the discovery of this error, and also a description of a good method for the preparation of the substance. This consists in warming a solution of platinum dichloride in potash with alcohol. Thus obtained, it is a soft, black, dull powder, which soils any surface on which it is rubbed. When thoroughly freed from alcohol by boiling with water, and dried in a vacuum over sulphuric acid, it absorbs oxygen from the air so rapidly that the mass becomes red hot. Platinum black is obtained also by dissolving alloys of platinum with other metals, such as copper and zinc, in nitric acid, when the platinum remains in the form of a black powder. This latter preparation, heated in open vessels to a temperature considerably below redness, deflagrates with a hissing noise, sometimes detonating like gunpowder. Platinum black is obtained also when platinum is precipitated by other metals from a dilute solution, or when such a solution is treated with reducing agents. Thus, for instance, if a solution of platinic chloride be allowed to drop into a boiling mixture of three volumes of glycerol and two of caustic potash of specific gravity 1·08, the black obtained possesses extremely active properties,[3] as does that prepared by the reduction of platinic chloride by means of formaldehyde.[4] A very active platinum black is also produced by adding a boiling solution of chloroplatinic acid neutralised with sodium carbonate to a boiling solution of sodium formate. By the action of dilute hydrochloric acid or boiling neutral liquids, it is converted into a greyish-black modification which is an intermediate stage between platinum black and spongy platinum and this is reconverted into the black variety by treatment with sodium formate in slightly alkaline solution.[1]

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[1] Feulgen, *Ber.*, 1921, **54**, [*B*], 360.

[2] *Pogg. Ann.*, 1829, **17**, 102.

[3] Zdrawkowitch, *Bull. Soc. chim.*, 1876, [2], **25**, 198.

[4] Loew, *Ber.*, 1890, **23**, 289.

According to Liebig, platinum black absorbs more than 800 times its volume of oxygen, whereas the black prepared by Mond, Ramsay, and Shields was found to absorb 100 volumes of oxygen. When brought into hydrogen 310 volumes were taken up, 200 of which united with the oxygen present to form water, whilst the remaining 110 were absorbed.[2] A certain amount of occluded oxygen can, however, coexist with occluded hydrogen in platinum black. It appears probable that platinous hydroxide is formed by the absorption of oxygen, since the heat of occlusion of oxygen by the black is almost identical with the heat of formation of platinous hydroxide.[3] Platinum black after absorbing oxygen dissolves partially in hydrochloric acid as platinous chloride, and the difference between the loss of weight of the black and the amount of platinum in solution also corresponds to the formation of this hydroxide.[4] Moreover, the black containing oxygen is able to bring about oxidising actions similar to those produced by platinous oxide, such as the liberation of iodine from potassium iodide, and the oxidation of arsenious to arsenic acid.[5] After frequent ignition in a mixture of combustible gas and air, the black becomes denser, approaching spongy platinum in its properties. Heat alone also affects its behaviour.[6] Platinum black is frequently used in organic chemistry as an oxidising agent, and it has been successfully applied in place of oxide of copper in organic analysis.[7]

Platinum black also absorbs hydrogen. It dissolves about 160 volumes, whereas platinum sponge does not absorb more than 1 volume. The maximum solubility is at 0°, there being a decrease on either side of this temperature; the solubility of hydrogen in platinum sponge, on the other hand, increases with temperature.[8] Owing to its power of absorbing hydrogen, platinum black brings about a number of reductions also,[1] especially the hydrogenation of unsaturated organic compounds. Its activity is reduced by previous heating, and it is thus possible, by first using inactive specimens prepared in this way, to reduce an unsaturated body in stages.[2] Platinum black is also an active catalyst in the decomposition of many organic bodies.[3]

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[1] Gutbier and Maisch, *Ber.*, 1919, **52**, [*B*], 1368.

[2] *Proc. Roy. Soc.*, 1895, **58**, 242.

[3] Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, 1897, **62**, 50.

[4] Engler and Wöhler, *Zeit. anorg. Chem.*, 1901, **29**, 1; Wöhler, *Ber.*, 1903, **36**, 3475.

[5] See also Raschig, *Zeit. angew. Chem.*, 1906, **19**, 1748, 2083; Bredig, *ibid.*, 1965; Luther, *ibid.*, 2049.

[6] See Wright and Smith, *Journ. Chem. Soc.*, 1921, **119**, 1683.

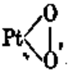
[7] Kopfer, *Journ. Chem. Soc.*, 1876, **29**, 660; 1877, **31**, 226; Dennstedt, *Ber.*, 1906, **39**, 1623.

[8] Gutbier and Maisch, *loc. cit.*

Platinum black also absorbs 60 volumes of carbon monoxide, at the ordinary temperature, and this is liberated on heating.[4]

Colloidal Platinum may be obtained as a dark brown solution by passing an electric arc between platinum wires immersed in water. It may also be prepared in a similar manner to colloidal gold and silver by reducing platinic chloride with hydrazine hydrate in the presence of sodium lysalbate as protective colloid, and on evaporating the solution and drying at 100° black, glistening scales of colloidal platinum are obtained which are soluble in water.[5] Similar solutions are obtained by reducing solutions of platinum salts with other reducing agents, and in the presence of other protective colloids.[6]

Colloidal platinum is a very active catalyst. It is capable of causing the union of oxygen and hydrogen.[7] It rapidly decomposes hydrogen peroxide and even minute quantities have a marked effect.[8] By measurement of the rate of decomposition in the presence of different colloids, their protective action on colloidal platinum has been determined and gelatine found to have the most effect.[9]

The colloidal solution absorbs hydrogen and is therefore very active in effecting reduction. Ferric salts may be reduced to the ferrous state and tetravalent titanium salts and molybdic acid are similarly reduced.[1] The solution is useful in the hydrogenation of unsaturated organic compounds; thus acetylene may be reduced to ethylene, and this, in turn, to ethane.[2] Many oils may likewise be hardened in much the same way as when nickel is used as catalyst. The colloid is incapable of bringing about hydrogenation even of the most reactive compounds if it is completely freed from oxygen, and such deoxygenated platinum may be revivified by shaking with oxygen. The catalytic activity has therefore been ascribed to the presence of an oxide, , which is assumed to form a compound with the hydrogen, and this compound readily gives it up to the reducible substance, and is again re-formed.[3] The oxides formed by fusing chloroplatinic acid with sodium nitrate are very active in the catalytic reduction of organic compounds.[4] The rôle of the oxide in catalysis has, however, been denied.[5]

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[1] See Loew and Asō, *Bull. Coll. Agr. Tokyo Imp. Univ.*, 1906, **7**, 1.

[2] Vavon, *Compt. rend.*, 1914, **158**, 409; 1921, **173**, 360.

[3] See Oliveri-Mandalà, *Gazz.*, 1920, **50**, ii, 81.

[4] Hemptinne, *Zeit. physikal. Chem.*, 1898, **27**, 429.

[5] Paal and Amberger, *Ber.*, 1904, **37**, 124.

[6] Gutbier, *Zeit. anorg. Chem.*, 1902, **32**, 347; *J. pr. Chem.*, 1905, [2], **71**, 358; Henrich, *Ber.*, 1903, **36**, 309; Garbowski, *ibid.*, 1215; Gutbier and others, *Kolloid Zeit.*, 1916, **18**, 1; *ibid.*, 1916, **19**, 298; Amberger, *ibid.*, 1913, **13**, 310.

[7] Ernst, *Zeit. physikal. Chem.*, 1901, **37**, 448; Paal and Hartmann, *J. pr. Chem.*, 1909, [2], **80**, 337; Paal and Schwarz, *ibid.*, 1916, [2], **93**, 106.

[8] Bredig, *Zeit. angew. Chem.*, 1898, 951; *Zeit. physikal. Chem.*, 1901, **38**, 122; Bredig and von Berneck, *ibid.*, 1899, **31**, 353; Bredig and Ikeda, *ibid.*, 1901, **37**, 1; Raudnitz, *ibid.*, 1901, **37**, 551; Rocasolano, *Compt. rend.*, 1920, **170**, 1502; *Anal. Fis. Quim.*, 1920, **18**, 361; MacInnes, *J. Amer. Chem. Soc.*, 1914, **36**, 878.

[9] Groh, *Zeit. physikal. Chem.*, 1914, **88**, 414; Iredale, *Journ. Chem. Soc.*, 1921, **119**, 109.

Colloidal platinum is "poisoned" by many substances, notably hydrogen sulphide, hydrogen cyanide, carbon monoxide and dioxide, and acetylene.[6] The catalytic activity is also gradually lost by exposure to ultra-violet light.[7]

The colloidal particles of platinum are spherical in shape[8] and are negatively charged. The solution is precipitated by electrolytes[9] and by many metals. The efficiency of the metal as a precipitant increases with its electropositive character, and the action is due to the absorption of metallic ions by the colloid particles the charges on which are thereby neutralised.[10] The sol is also coagulated by exposure to sunlight[11] or ultra-violet light.[12]

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[1] Eggert, *Zeit. Elektrochem.*, 1914, **20**, 370; 1915, **21**, 349; Paal and Büttner, *Ber.*, 1915, **48**, 220; Loew and Asō, *Bull. Coll. agr. Tokyo Imp. Univ.*, 1906, **7**, 1.

[2] Paal and Schwarz, *Ber.*, 1915, **48**, 994, 1195.

[3] Willstätter and Jaquet, *Ber.*, 1918, **51**, 767; Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, **54**, *B*, 113. See Rocasolano, *Compt. rend.*, 1921, **173**, 41, 234.

[4] Voorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397.

[5] Skita, *Ber.*, 1922, **55** [B], 139.

[6] Bredig and Ikeda, *Zeit. physikal. Chem.*, 1901, **37**, 1; Paal and Schwarz, *Ber.*, 1915, **48**, 1195; Krüger and Taege, *Zeit. Elektrochem.*, 1915, **21**, 562.

[7] Farmer and Parker, *J. Amer. Chem. Soc.*, 1913, **35**, 1524.

[8] Gans and Calatroni, *Ann. Physik*, 1920, [4], **61**, 465.

[9] Pappadà, *Zeit. Chem. Ind. Kolloide*, 1911, **9**, 270.

[10] Spear and Kahn, *J. Amer. Chem. Soc.*, 1918, **40**, 181.

[11] Ganguly and Dhar, *Kolloid Zeit.*, 1922, **31**, 16.

[12] Spear, Jones, Neave, and Schlager, *J. Amer. Chem. Soc.*, 1021, **43**, 1385.

Platinum is scarcely oxidised at any temperature by oxygen, water, or nitric acid. If very thin platinum foil be heated in oxygen for some weeks at 420–450° it becomes covered with a small quantity of platinous oxide, whilst platinum sponge is more quickly converted into this oxide in the same manner.[1]

It is appreciably attacked by sulphuric acid[2] at 250°, although very slightly so below 200°, and dissolves to a small extent when used for the electrodes in the electrolysis of sulphuric acid, especially when alternating currents are employed.[3] The dissolving of platinum by sulphuric acid is accounted for by the presence of oxygen formed by dissociation of the acid, and is prevented by the presence of reducing agents, such as sulphur dioxide or arsenious or antimonious oxides.[4] It is not attacked by sulphur alone, although action takes place if alkalis are present. These latter, as well as nitre, oxidise the metal, and for this reason fusion with alkalis or nitre ought not to be performed in platinum vessels.[5] It dissolves in potassium cyanide solution in the absence of oxygen with evolution of hydrogen, the amount dissolved being very small in the cold but increasing on heating.[6] Alkali cyanides should not be fused in contact with platinum, as these likewise attack the metal. It is also inadvisable to expose platinum vessels to direct contact with burning charcoal, as the silicon reduced from the charcoal-ash unites with the metal, making it brittle and liable to crack. Especially to be avoided is contact at a high temperature with compounds of the easily reducible metals, as these readily form fusible alloys with the platinum. Phosphorus and arsenic also combine with heated platinum. When platinum vessels are heated over a smoky flame, or in one in which the supply of air is insufficient to bring about complete combustion, such as the internal zone of a Bunsen burner, the surface of the platinum becomes disintegrated, possibly owing to the successive formation and decomposition of compounds of the metal with carbon from the flame, or, more probably, owing to the action of the carbon disulphide present in the gas, for platinum takes up sulphur from this compound even at 100°.[1]

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[1] Wöhler, *Ber.*, 1903, **36**, 3475.

[2] Conroy, *J. Soc. Chem. Ind.*, 1903, **22**, 465.

[3] Margules, *Ann. Phys. Chem.*, 1898, [2], **65**, 629; **66**, 540; Ruer, *Zeit. Elektrochem.*, 1903, **9**, 235; 1905, **11**, 10; Brochet and Petit, *Compt. rend.*, 1905, **140**, 655; *Zeit. Elektrochem.*, 1905, **11**, 441; Senter, *Trans. Faraday Soc.*, 1907, **2**, 1.

[4] McCay, *Eighth Inter. Cong. App. Chem.*, 1912, **1**, 351.

[5] See Nicolardot and Chatelot, *Bull. Soc. chim.*, 1919, [4], **25**, 4.

[6] Glaser, *Zeit. Elektrochem.*, 1903, **9**, 11; Wöhler, *Ber.*, 1903, **36**, 3475.

The best method of cleaning a platinum crucible is to fuse in it some potassium bisulphate (Gmelin), and in order to test whether a new platinum crucible be of proper quality it is first boiled with hydrochloric acid and afterwards with pure nitric acid. If none of the metal be dissolved the platinum is good. The surface of a platinum crucible is best cleaned by being rubbed with moist animal charcoal.

Platinum forms alloys with a number of other metals and also an amalgam with mercury.

Platinum is largely used in dentistry, and also in jewellery, principally for the setting of stones. For both these purposes, however, it is now being displaced by palladium. It is also employed largely in the electrical industry, and its salts are applied in photography for the preparation of printing papers which yield exceptionally permanent and beautiful prints. It is also employed as a catalyst in many reactions, notably in the manufacture of oleum (Vol. I., p. 433). It is used for protecting other metals, and a pure white deposit is obtained by using a boiling solution of 4 grams of chloroplatinic acid, 20 grams of ammonium phosphate, 90 grams of sodium phosphate, and 5 grams of sodium chloride per litre.[2] The electro-deposition of platinum is known as "platinising." The process is used to obtain a velvety-black coating on the electrodes of conductivity cells by employing the following solution: 3 grams of platinic chloride, 0·02–0·03 gram of lead acetate, and 100 c.c. of water.

COMPOUNDS OF PLATINUM.

PLATINUM AND OXYGEN.

640 Three oxides of this metal are definitely known: platinum monoxide or platinous oxide, PtO, giving rise to the platinous salts; platinum dioxide or platinic oxide, PtO_2, giving rise to the platinic salts; and the trioxide, PtO_3. In addition, a sesquioxide, Pt_2O_3, and an oxide, Pt_3O_4, have been described, but doubt has been thrown on their existence.

Platinum Monoxide, PtO, is obtained as a grey powder by the careful ignition of the hydroxide, or as a violet powder by igniting the compound of platinic oxide and lime (*vide inf.*), and treating the residue with nitric acid. It is also probably formed to some extent as already mentioned when platinum is heated for some time in oxygen (Wöhler). When strongly heated it passes into the metal, deflagrating when heated with charcoal. It is reduced to platinum black when heated with aqueous formic acid, CH_2O_2, with violent evolution of carbon dioxide.

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[1] Mylius and Hüttner, *Zeit. anorg. Chem.*, 1916, 95, 257.

[2] Nikolaus, *Zeit. Elecktrochem.*, 1914, 21, 103.

Platinous Hydroxide, $Pt(OH)_2$, is obtained by decomposing the dichloride with hot caustic potash. The whole of the chlorine cannot, however, be removed in this way, and if caustic soda be employed, a product is obtained from which the soda cannot be completely washed out (Liebig). It is prepared in the pure state by mixing one part of potassium platinochloride, K_2PtCl_4, with twelve parts of water, adding the exact quantity of dilute caustic soda necessary for decomposition, and heating the mixture to boiling until the alkaline solution has become neutral. The hydroxide retains its water in a remarkable manner; one sample contained 6·6 per cent. of water after heating for several days at 405° (Wöhler).[1] It dissolves in hydrochloric, hydrobromic, and sulphurous acids, but not in other oxy-acids. Boiling caustic potash decomposes it into metal and the dioxide. It is an oxidising agent and acts as a weak base, of which the halogen salts, as well as a few double salts of the oxy-acids, have been prepared.

Platinum Dioxide, PtO_2, is obtained as a black powder by gently heating the corresponding hydroxide.

Platinum Hydroxide or *Platinic Hydroxide* is prepared by boiling a solution of platinic chloride with caustic potash, when a basic double salt is precipitated, and this is treated with acetic acid in order to dissolve out the alkali. In this way it is obtained as an almost white precipitate, which on drying becomes yellow. This is termed *platinic acid* and probably has the composition[2] $H_2Pt(OH)_6 = PtO_2,4H_2O$, analogous to platinichloric acid, H_2PtCl_6. Platinic hydroxide acts both as a weak base and as an acid-forming oxide. It dissolves in alkalis and the solutions deposit crystalline *platinates* such as $K_2Pt(OH)_6$ isomorphous with the stannates[3]; they do not lose water at 100–110°, and their solutions give with silver acetate a precipitate of

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[1] *Zeit. anorg. Chem.*, 1904, **40**, 423.

[2] Bellucci, *Atti R. Accad. Lincei*, 1903, [5], **12**, ii., 635; Wöhler, *Zeit. anorg. Chem.*, 1904, **40**, 423; compare Blondel, *Ann. Chim. Phys.*, 1905, [8], **6**, 81.

[3] Bellucci and Parravano, *Atti R. Accad. Lincei*, 1905, [5], **14**, i., 459.

$Ag_2Pt(OH)_6$. A reddish-yellow, partially crystalline powder of the composition $Na_2O,3PtO_2,6H_2O$ is obtained when a clear aqueous mixture of platinichloric acid and sodium carbonate is exposed to sunshine, or when the mixture is heated for some time at 100°. The aqueous solution of the two salts may also be evaporated to dryness, and the residue boiled out with water, when a denser precipitate of the same compound is obtained having an ochre-yellow colour. A compound of the composition $Na_2O,5PtO_2,9H_2O$ has also been obtained (Blondel). When an excess of lime water is added to a solution of platinic chloride and the mixture exposed to sunlight, a white or yellowish pulverulent precipitate falls down, to which the name of calcium platinate has been given,[1] its composition corresponding approximately to the formula $CaPt_2O_5,CaCl_2,7H_2O$. If the hydroxide is boiled with a solution of a polymolybdate, or a polytungstate, salts are formed of the complex acids, platinmolybdic acid $H_8PtMo_{10}O_{36}$, and platintungstic acid, $H_8PtW_{10}O_{36}$. These acids and their salts form yellow or greenish crystals.[2]

Platino-platinic Oxide, Pt_3O_4, is obtained as a black, insoluble powder by heating sodium platinichloride with sodium carbonate and extracting with water,[3] whilst *platinum sesquioxide*, Pt_2O_3, is obtained as a dark brown powder[4] by heating spongy platinum with sodium dioxide, neutralising the alkali, washing, and drying at 450°. According to Wöhler, however, these substances are not definite oxides; only two oxides of platinum exist, and these readily form colloidal solutions and retain foreign matter on precipitation.

Platinum Trioxide, PtO_3, is obtained by the electrolysis of a solution of platinic hydroxide in 2*N*-potassium hydroxide. A compound of the composition $K_2O,3PtO_3$ is thus obtained, which, when treated with cold acetic acid, yields the trioxide as a brown powder. It readily loses oxygen and slowly evolves chlorine from dilute hydrochloric acid.[5]

PLATINUM AND THE HALOGENS.

641 *Platinum Tetrafluoride*, PtF_4, is formed when platinum wire is heated to dull redness in a current of fluorine. It is thus

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[1] Herschel, *Phil. Mag.*, 1832, [2], 1, 58.

[2] Gibbs, *Ber.*, 1877, 10, 1384.

[3] Jörgensen, *J. pr. Chem.*, 1877, [2], 16, 344.

[4] Dudley, *Amer. Chem. J.*, 1902, 28, 59.

[5] Wöhler and Martin, *Ber.*, 1909, 42, 3326.

obtained as a deep red-coloured, fused mass, which yields chamois-yellow crystals. It is extremely hygroscopic, and when added to water it first gives a tawny coloration, then heat is rapidly developed and decomposition occurs with formation of hydrogen fluoride and hydrated platinum dioxide. Very dilute solutions are more stable, but the same reaction takes place immediately if they are heated. When the anhydrous substance is heated it yields fluorine and leaves crystalline platinum.[1]

In the preparation of the tetrafluoride the *difluoride*, PtF_2, is also formed in small quantities as a greenish-yellow, insoluble substance.

Phosphorus pentafluoride acts on spongy platinum at a red heat to form volatile crystals of the formula PF_3,PtF_2.[2]

Platinum Monochloride, PtCl.—When a solution of potassium platinichloride in 10,000 parts of water is heated for some days, a yellow, non-crystalline precipitate is formed which probably consists of hydrated platinum monochloride,[3] PtCl.

Platinous Chloride or *Platinum Dichloride*, $PtCl_2$, is formed when platinichloric acid, H_2PtCl_6, obtained by dissolving the metal in aqua regia and crystallising, is heated to 300°, or when spongy platinum is heated in a current of dry chlorine to between 240° and 250°.[4] It is a greenish-grey powder, having a specific gravity of 5·87. It is not readily moistened with water, and is insoluble in this liquid. On heating it decomposes into platinum and chlorine.[5]

Platinum dichloride unites with phosphorus trichloride to form the compound $PtCl_2,PCl_3$, which is obtained by heating spongy platinum with pentachloride of phosphorus to 250°. The product is easily soluble in benzene or chloroform, and crystallises therefrom in fine brown needles. When these are dissolved in water and the solution is evaporated in a vacuum, orange-yellow, deliquescent prisms of *chloroplatinophosphorous acid*, $PtCl_2,P(OH)_3$, are obtained. This has an acid metallic taste, and yields a white precipitate with silver nitrate and a yellow one with lead acetate. Corresponding salts of the alkali metals have not been prepared, since hydroxides and carbonates decompose the acid.

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[1] Moissan, *Compt. rend.*, 1889, 109, 807; *Ann. Chim. Phys.*, 1891, [6], 24, 237.

[2] Moissan, *Bull. Soc. chim.*, 1891, [3], 5, 454.

[3] Sonstadt, *Proc. Chem. Soc.*, 1898, 25. See also Wöhler and Streicher, *Ber.*, 1913, 46, 1591.

[4] Schützenberger, *Ann. Chim. Phys.*, 1870, [4], 21, 351.

[5] See Shenstone, *Journ. Chem. Soc.*, 1892, 61, 450.

The foregoing compound readily takes up another molecule of phosphorus trichloride, forming $PtCl_2,2PCl_3$, which may likewise be crystallised from chloroform or benzene in large, deliquescent prisms; these melt at 160°, and when strongly heated give off phosphorus trichloride. If they are allowed to remain in contact with water at a winter temperature, or if their solution be evaporated at a low temperature in a vacuum, very deliquescent, yellow needles are obtained of *chloroplatinodiphosphorous acid*, $PtCl_2,2P(OH)_3$, and this readily undergoes decomposition at 12°, with evolution of hydrogen chloride, into the compound $PtClOP_2(OH)_5$. This latter forms white crystals, is less deliquescent than the former compounds, and when heated to 150° is converted into a light yellow, non-deliquescent powder having the composition $PtClO_2P_2(OH)_3$. The solution of this compound, like the preceding, is precipitated by silver nitrate.[1]

Carbonyl Platinochlorides or *Chloroplatinites.*—When platinous chloride is heated to a temperature of 250° in a current of carbon monoxide there are formed: $PtCl_2,2COCl_2$, $PtCl_2,CO$, $PtCl_2,2CO$, $2PtCl_2,3CO$. The last named is produced in largest quantity and is obtained pure by boiling the crude product with carbon tetrachloride. In this way fine orange-yellow needles melting at 130° are obtained; these when heated to from 250° to 260° in dry carbon dioxide yield the compound $PtCl_2,CO$ in fine needles which melt at 194° and may be partially sublimed in a current of dry carbon dioxide at 240°. At 300° they decompose into carbonyl chloride, $COCl_2$, and platinum. When this compound, or the crude product, is heated to 150° in carbon monoxide, the compound $PtCl_2,2CO$ sublimes in white needles which melt at 142°.[2] All these compounds are decomposed by water to give the metal, carbon dioxide, and hydrochloric acid.

642 *The Platinochlorides* or *Chloroplatinites.*—The solution of platinous chloride in hydrochloric acid may be regarded as *platinochloric* or *chloroplatinous acid*, $H_2[PtCl_4]$. The potassium salt is the usual starting point for the preparation of this compound and its salts.[3]

Potassium Platinochloride; K_2PtCl_4.—This salt, which was first prepared by Magnus,[1] is easily obtained by adding moist cuprous chloride to a thick paste of potassium platinichloride, K_2PtCl_6, and water, in such quantity that a small portion remains unreduced. On cooling the filtered liquid, the greater portion of the platinochloride separates out, the mother-liquor yielding a second crop on concentration, whilst the remainder of the salt is precipitated from the last portion of the liquor with alcohol. These various crops are then washed with alcohol, and the pure salt is obtained by recrystallisation from hot water. It forms soft, rose-coloured, crystalline fibres. It may also be prepared by reducing a hot solution of platinichloric acid with sulphur dioxide until a sample gives no precipitate with ammonium chloride, and then adding a hot solution of potassium chloride. On cooling, potassium platinochloride separates out and is washed with alcohol and dried in absence of light.[2] When the requisite quantity of platinichloric acid is added to the hot saturated solution of this salt potassium platinichloride is precipitated and an almost pure solution of platinochloric acid, H_2PtCl_4, is obtained. The same acid is produced by treating the barium salt with dilute sulphuric acid. On evaporation in a vacuum over sulphuric acid or caustic potash, a solid compound separates out which dries with loss of hydrogen chloride, forming a brown, amorphous mass of $H_2Pt(OH)Cl_3,H_2O$.[3] By dissolving oxides, hydroxides, carbonates, or chlorides in the acid a series of compounds is obtained (Nilson).

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[1] Schützenberger, *Bull. Soc. chim.*, 1872, [2], 17, 482; 18, 153; Rosenheim and Löwenstamm, *Zeit. anorg. Chem.*, 1903, 37, 394.

[2] Schützenberger, *Ann. Chim. Phys.*, 1868, [4], 15, 100, and 1870, 21, 325; Pullinger, *Journ. Chem. Soc.*, 1891, 59, 598.

[3] Thomsen, *J. pr. Chem.*, 1877, [2], 15, 294.

Ammonium Platinochloride, $(NH_4)_2PtCl_4$, described first by Vauquelin and afterwards by Peyronne, crystallises from solution in hot water in large, red, four-sided prisms or in thin tablets.

Most of the other platinochlorides crystallise with water in fine red or brown crystals which are often deliquescent; some, such as the silver salt, Ag_2PtCl_4, and the lead salt, $PbPtCl_4$, are flesh-coloured precipitates.

Platinum Trichloride, $PtCl_3$ is obtained by heating platinic chloride in dry chlorine at 390°. It is a dark green, nearly black powder, which dissolves very slowly in cold water but more readily on boiling to give a reddish-brown solution. Hot concentrated hydrochloric acid decomposes it into a mixture of the dichloride and tetrachloride.[4]

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[1] *Pogg. Ann.*, 1828, 14, 241.

[2] Klason, *Ber.*, 1904, 37, 1360.

[3] Nilson, *J. pr. Chem.*, 1877, [2], 15, 260.

[4] Wöhler and Martin, *Ber.*, 1909, 42, 3958.

Platinic Chloride or *Platinum Tetrachloride*, $PtCl_4$.—When metallic platinum is heated in a current of chlorine it is attacked and this compound is slowly formed. The action diminishes when the temperature is raised, as the tetrachloride decomposes into metal and chlorine at 370°.[1] If, however, the temperature be raised to 1300°, the formation of tetrachloride recommences; and if an excess of chlorine be employed and the temperature raised to 1700°, the action becomes rapid and a yellow sublimate of tetrachloride is deposited.[2] The same reaction occurs if a spiral platinum wire be heated by an electric current nearly to its melting point in a stream of chlorine. At the thick end of the wire crystals of metallic platinum are deposited. These are not formed owing to any volatility of the metal, but are produced by the alternate production and decomposition of the tetrachloride.[3] The anhydrous chloride is formed also when crystalline platinichloric acid is dried over sulphuric acid and then heated to 369° in a current of chlorine,[4] or at 165° in a current of hydrogen chloride.[5]

By mixing solutions of aqueous platinichloric acid and silver nitrate in the proportion of one molecule of the former to two of silver nitrate, a precipitate of silver platinichloride is thrown down, which is decomposed by hot water into silver chloride and platinic chloride. The yellowish-red solution yields on evaporation over sulphuric acid fine, red, apparently monoclinic, crystals of the composition $PtCl_4,5H_2O$. They are not deliquescent, and their concentrated solution is only slowly precipitated by ammonium chloride on standing.[6] The crystals are converted by ammonia into the acid $PtCl(OH)_3$.[7] According to Miolati, platinum tetrachloride in aqueous solution is present as the dibasic acid, $H_2PtCl_4(OH)_2$, and salts have been prepared corresponding to this acid which are amorphous powders.[8]

Hydrates containing one, four, and seven molecules of water have also been prepared.

Platinichloric Acid or *Chloroplatinic Acid*, $H_2[PtCl_6]$.—This compound, which is often erroneously called platinum chloride, is obtained by dissolving the metal in aqua regia and evaporating with hydrochloric acid until all nitric acid is removed.[1] It crystallises in brownish-red, very deliquescent prisms having the composition $H_2PtCl_6,6H_2O$. If the solution be repeatedly evaporated with aqua regia, nitrosoplatinic chloride, $(NO)_2PtCl_6$, is formed. This crystallises in small, orange-coloured cubes and is very deliquescent, dissolving in water with evolution of nitric oxide. Chloroplatinic acid made by the action of aqua regia on platinum may therefore be contaminated with this compound if the evaporation with hydrochloric acid be not carried far enough. Pure chloroplatinic acid may be obtained by treating platinum black, which has not been ignited, with hydrochloric acid at 50° to 60°, and slowly adding hydrogen peroxide when chlorine is evolved and the platinum passes into solution.[2] Platinum sponge may also be dissolved in hydrochloric acid saturated with chlorine.[3] Platinum in any form is readily attacked by a mixture of chloric and hydrochloric acids.[4] The acid may also be prepared by electrolysing a suspension of finely divided platinum in concentrated hydrochloric acid between platinum electrodes, when the chlorine evolved at the anode attacks the finely divided metal, forming platinic chloride, which dissolves in the hydrochloric acid to form chloroplatinic acid.[5]

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[1] Wöhler and Streicher, *Ber.*, 1913, 46, 1591.

[2] Troost and Hautefeuille, *Compt. rend.*, 1887, 84, 946; Langer and Meyer, *Pyrochem. Untersuchungen*, p. 57.

[3] Hodgkinson and Lowndes, *Nature*, 1888, 38, 6.

[4] Pigeon, *Compt. rend.*, 1890, 110, 77; 1891, 112, 1218; *Ann. Chim. Phys.*, 1894, [7], 2, 433; Gutbier and Heinrichs, *Zeit. anorg. Chem.*, 1913, 81, 378.

[5] Pullinger, *Journ. Chem. Soc.*, 1892, 61, 422.

[6] Norton, *ibid.*, 1872, 25, 660.

[7] Jörgensen, *J. pr. Chem.*, 1877, [2], 16, 345.

[8] *Zeit. anorg. Chem.*, 1900, 22, 445. See also Kohlrausch, *Zeit. physikal. Chem.*, 1908, 33, 257.

The hydrogen in platinichloric acid can be readily replaced by metals, giving a series of crystalline salts termed the *platinichlorides* or *chloroplatinates*, of which the most important are those of the alkali metals, their widely differing solubilities rendering them very valuable in analytical chemistry.

Potassium Platinichloride or *Potassium Chloroplatinate*, K_2PtCl_6, is thrown down, on the addition of potash or a potassium salt to the acid, in the form of a yellow, crystalline precipitate which is deposited from solution in hot water in the form of small, reddish-yellow octahedra, having a specific gravity of 3·586. It undergoes hydrolysis, very rapidly even in the dark with concentrated solutions, but only on exposure to light in dilute solution.[6]

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[1] See Tingle and Tingle, *J. Soc. Chem. Ind.*, 1916, 35, 77.

[2] Rudnick and Cooke, *J. Amer. Chem. Soc.*, 1917, 39, 633.

[3] Dittmar and MacArthur, *Trans. Roy. Soc. Edin.*, 1889, 33, [2], 561.

[4] Zappi, *Anal. Fis. Quim. Argentina*, 1915, 3, 68.

[5] Weber, *J. Amer. Chem. Soc.*, 1908, 30, 29.

[6] Archibald, *J. Chem. Soc.*, 1920, 117, 1104.

It is insoluble in a saturated solution of potassium chloride as well as in alcohol. It dissolves in caustic potash and is precipitated from the solution on the addition of acids.

Sodium Platinichloride, $Na_2PtCl_6,6H_2O$, is obtained by evaporating the acid with common salt, when light red, triclinic prisms or tablets are deposited which have a specific gravity of 2·499. These become anhydrous at 100°, falling to a yellowish-red powder, readily soluble in water and alcohol.

Lithium Platinichloride, $Li_2PtCl_6,6H_2O$, crystallises in large, efflorescent, orange-yellow plates, easily soluble in water and in a mixture of alcohol and ether, but not in pure ether.

Rubidium and Cæsium Platinichlorides, Rb_2PtCl_6 and Cs_2PtCl_6, closely resemble the potassium salt, but are less soluble. One hundred parts of water dissolve the following amounts of the three salts:

At	20°	40°	60°	80°	100°
K_2PtCl_6 . . .	1·12	1·76	2·61	3·79	5·18 parts.
Rb_2PtCl_6 . .	0·141	0·166	0·258	0·417	0·634 „
Cs_2PtCl_6 . .	0·070	0·142	0·213	0·291	0·377 „

Ammonium Platinichloride, $(NH_4)_2PtCl_6$, is obtained by precipitating the acid with an ammonium salt as a lemon-yellow, crystalline powder which crystallises from hot water in orange-yellow octahedra; these have a specific gravity of 3·0, and are indistinguishable in appearance from the potassium salt. One hundred grams of water dissolve 0·365 gram of the salt at 0° and 3·25 grams at 100°.[1] It is not soluble either in alcohol or ether, and scarcely soluble in a solution of ammonium chloride. On heating, it decomposes without fusion, leaving pure platinum sponge behind.[2]

Other acids and their corresponding salts have been prepared which may be regarded[3] as being intermediate between platinic acid, $H_2[Pt(OH)_6]$, and platinichloric acid, $H_2[PtCl_6]$, and to these compounds may be ascribed formulæ such as $H_2[Pt(OH)_5Cl]$ and $H_2[PtCl_5(OH)]$.

Platinous Bromide, $PtBr_2$, is obtained by heating platinibromic acid to 280°, and forms a brown mass which dissolves with a brownish-red colour. If boiling saturated solutions of potassium platinichloride and potassium bromide are mixed, double decomposition occurs, and the potassium chloride may be separated from the *potassium platinobromide*, K_2PtBr_4, by crystallisation. The latter forms large, nearly black pyramids or brownish-red needles (Thomsen). It unites with carbon monoxide, forming a compound, $PtBr_2,CO$ (Pullinger).

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[1] Archibald and Kern, *Trans. Roy. Soc. Canada*, 1917–18, [3], 11, 7.

[2] See Wichers, *J. Amer. Chem. Soc.*, 1921, 43, 1268.

[3] Miolati and Bellucci, *Atti R. Accad. Lincei*, 1900, [5], 9, ii., 140; 1903, [5], 11, ii., 241, 271; Ruff and Jeroch, *Ber.*, 1913, 46, 920.

Platinic Bromide, $PtBr_4$.—Bromine acts upon platinum at different temperatures in the same way as chlorine. The tetrabromide is best obtained by heating spongy platinum with bromine and hydrobromic acid to 180°, evaporating the solution, and drying the residue at 180°. It is a brownish-black, deliquescent powder, nearly insoluble in water, but readily soluble in alcohol and ether, yielding a brown solution.[1] When platinum is dissolved in a mixture of nitric and hydrobromic acids, and the concentrated solution allowed to evaporate over quick lime, dark red, monoclinic prisms of *platinibromic acid*, $H_2PtBr_6,9H_2O$, are deposited, which are very deliquescent. The compound is also made in the pure state by evaporating pure platinic chloride several times with concentrated hydrobromic acid on the water-bath.[2] This acid gives rise to a series of platinibromides corresponding to the platinichlorides, most of which possess a red colour.

Platinous Iodide, PtI_2, is formed by warming the chloride with a solution of potassium iodide, or, with liberation of iodine, when excess of potassium iodide is added to a solution of potassium platinichloride. This reaction has been used as a method of estimating platinum.[3] It is a black powder closely resembling lamp-black in appearance. It forms a carbonyl, PtI_2,CO.

Platinic Iodide, PtI_4, is a black or brownish-black, amorphous powder obtained by the action of hydriodic acid on a soluble platinichloride. *Platiniodic acid*, $H_2PtI_6,9H_2O$, easily decomposes into water, hydriodic acid, and platinic iodide. The *platiniodides* are brown, and possess a metallic lustre; they are soluble in water, and are very unstable, giving off iodine at a temperature below 100°.

PLATINUM AND THE ELEMENTS OF THE SULPHUR GROUP.

643 *Platinum Monosulphide*, PtS, is formed when platinum sponge is heated with sulphur in a vacuous glass tube, or when

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[1] V. Meyer and Züblin, *Ber.*, 1880, **13**, 404; Halberstadt, *ibid.*, 1884, **17**, 2962.

[2] Gutbier, Krauss, and von Müller, *Chem. Zentr.*, 1914, [1], 1162.

[3] Peterson, *Zeit. anorg. Chem.*, 1898, **19**, 59.

platinous chloride is fused with sodium carbonate and sulphur, and the mass extracted with water. It forms a green powder or a mass of glistening needles.[1] When heated in the air it decomposes, leaving a residue of platinum, and when ignited in hydrogen it yields sulphuretted hydrogen and spongy platinum. The carbonyl, PtS,CO, is precipitated by the action of hydrogen sulphide on a solution of $PtCl_2,CO$.

Platinum Disulphide, PtS_2, is formed as a steel-grey powder by heating ammonium platinichloride with sulphur to a dark red heat. When sulphuretted hydrogen is passed through a solution of a platinic salt a black precipitate of sulphide is first formed, but this by further action of the gas becomes light brown, from formation of hydrogen platinum sulphide, a compound which on exposure to the air again gives off sulphuretted hydrogen. The disulphide may be obtained pure by precipitating a solution of potassium platinichloride at 90° with sulphuretted hydrogen, and drying at 70–80° in an atmosphere of nitrogen.[2] The precipitation of platinum by hydrogen sulphide is not quantitative owing to the formation of a stable colloidal solution of the sulphide. The hydrosol is, however, converted into an insoluble hydrogel in the presence of magnesium chloride.[3]

Platinum disulphide combines with basic sulphides and therefore dissolves in the sulphides of the alkali metals.

Potassium Platinothioplatinate, $K_2Pt_4S_6 = K_2S,3PtS,PtS_2$, is obtained by fusing together platinum sponge, potash, and sulphur, and lixiviating the mass with water. It then separates in the form of hard, six-sided tablets, which on heating in the air burn like tinder. Dilute sulphuric acid converts it into $H_2Pt_4S_6$, and this on exposure to air oxidises to *platinum sesquisulphide*, Pt_2S_3, forming a steel-grey, crystalline powder.

Di-sodium Platinothioplatinate, $Na_4Pt_3S_4 = 2Na_2S,2PtS,PtS_2$, is obtained in a similar way to the preceding compound, and forms pale copper-red, thin, crystalline needles which are converted by hydrochloric acid, without alteration of form, into a reddish-brown compound, $H_4Pt_3S_4$, which oxidises extremely quickly in the air to give the sesquisulphide.[4]

A compound of the formula $PtS_{15}(NH_4)_2,2H_2O$ has been prepared by the action of ammonium polysulphide on platinichloric acid,[1] and forms large, red, rhombic crystals.

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[1] Debray and Deville, *Compt. rend.*, 1879, 89, 587.

[2] Antony and Lucchesi, *Gazz.*, 1896, 26, i., 211.

[3] Ivanov, *J. Russ. Phys. Chem. Soc.*, 1916, 48, 527. See also Gaze, *Chem. Zentr.*, 1913, [1], 464.

[4] Schneider, *Pogg. Ann.*, 1866, 138, 604.

Potassium Platinosulphite, $K_6Pt(SO_3)_4,2H_2O$.—A solution o potassium platinochloride becomes decolorised when warme with acid potassium sulphite, the above salt separating out fro the solution in yellowish or colourless needles. Sodium salts precipitate *sodium platinosulphite*, $Na_6Pt(SO_3)_4,7H_2O$, from thi solution in microscopic needles. *Ammonium platinosulphite* $(NH_4)_6Pt(SO_3)_4$, is obtained by similar means.

These compounds must be regarded as salts of complex acids since they do not show the ordinary reactions for either platinum or sulphurous acid.

Sodium platinothiosulphate, $Na_6Pt(S_2O_3)_4,10H_2O$.—Reductio of sodium platinichloride with excess of sodium hyposulphit gives a reddish-brown solution which on evaporation yields firs a reddish-brown precipitate of complex sodium platinosulphite with sodium platinothioplatinate, $Na_2Pt_4S_6$, then reddish-brow crystals of $Na_4Pt(SO_3)_2(OH)_2,H_2O$ and, finally, bright yellow crystals of sodium platinothiosulphate.[2]

Platinic Sulphate, $Pt(SO_4)_2$, is obtained as a brown mass b acting on the hydroxide or chloride with sulphuric acid an evaporating the solution.

Platinum Selenide.—Spongy platinum when heated unite with selenium with incandescence, forming a grey, infusibl powder; this, when heated before the blowpipe, loses the whol of its selenium. Platinum also unites with tellurium[3] to form the tellurides, Pt_2Te, $PtTe$, and $PtTe_2$.

PLATINUM AND THE ELEMENTS OF THE NITROGEN GROUP.

644 *The Platinonitrites* or *Nitrito-platinites*.—These compounds are probably analogous in composition to the ammoniacal derivatives corresponding to the platinous salts (p. 1481) and behave, not as double salts, but as salts of a complex acid, since they do not show the usual reactions either of platinum salts or nitrites. They were first described by Lang,[4] and afterwards investigated more completely by Nilson.[5]

Potassium Platinonitrite, $K_2Pt(NO_2)_4$, is obtained when solutions of potassium nitrite and potassium platinochloride are warmed together. It is deposited in the form of small, glistening, six-sided prisms, which dissolve in 27 parts of water at 15°, and at a higher temperature in a smaller quantity. Alkalis do not precipitate platinum oxide, and sulphuretted hydrogen does not precipitate sulphide of platinum from its solution. When the solution is allowed to evaporate spontaneously, rhombic tablets having the composition $K_2Pt(NO_2)_4,2H_2O$ separate out, which effloresce rapidly. It readily combines with a molecule of chlorine or bromine,[1] and forms with dry liquid nitrogen peroxide the compound $K_2Pt(NO_2)_4,N_2O_4$, and with cold concentrated hydrochloric acid the compound $K_2Pt(NO_2)_4,HCl$.[2]

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[1] Hofmann and Höchtlen, *Ber.*, 1903, **36**, 3090.

[2] Sailer, *Zeit. anorg. Chem.*, 1921, **116**, 209.

[3] Roessler, *Zeit. anorg. Chem.*, 1897, **25**, 405.

[4] *J. pr. Chem.*, 1861, **83**, 415.

[5] *Ber.*, 1876, **9**, 1722; 1877, **10**, 934.

Silver Platinonitrite, $Ag_2Pt(NO_2)_4$, is obtained when solutions of the potassium salt and silver nitrate are mixed. On recrystallising the precipitated salt from hot water, large, yellow, glistening, monoclinic prisms are obtained, which on heating decompose with incandescence and detonation.

Barium Platinonitrite, $BaPt(NO_2)_4,3H_2O$, is obtained by decomposing the silver salt with barium chloride. It crystallises from solution in hot water in colourless octahedra. If this salt be decomposed by dilute sulphuric acid, and the solution evaporated in a vacuum over caustic potash, microscopic crystals having the colour of chromium trioxide separate out; these possess, according to Lang, the composition $H_2Pt(NO_2)_4$. Nilson however, was unable to obtain this compound. The solution yielded, on evaporation, a gummy mass and a green, glistening residue having the composition $H_4Pt_3O(NO_2)_8,2H_2O$, and this on neutralisation with potash and evaporation, yielded the potassium salt, $K_4Pt_3O(NO_2)_8,2H_2O$, in oblique, four-sided, glistening, light-yellow tablets.

Fulminating Platinum.—E. v. Meyer has examined a series of explosive compounds obtained by acting upon ammonium platinichloride with potash, the existence of some of which was pointed out long ago by Proust and Döbereiner. Their constitution is as yet unknown; the yellow precipitate obtained on heating ammonium platinichloride with potash has the composition $PtClNH_6O_2$.[3]

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[1] Blomstrand, *J. pr. Chem.*, 1871, [2], 3, 207; Vèzes, *Compt. rend.*, 1891, **112**, 616; **113**, 696.

[2] Miolati, *Atti R. Accad. Lincei*, 1896, [5], **5**, ii., 355.

[3] *J. pr. Chem.*, 1878, [2], **18**, 305.

AMMONIACAL PLATINUM COMPOUNDS.

645 As already stated (p. 1423), the various platinum salts are capable of forming complex compounds with ammonia. The first of these compounds was obtained in 1828 by Magnus[1] by the action of ammonia on platinous chloride as a green, insoluble salt having the empirical composition $PtCl_2(NH_3)_2$ which is usually known as Magnus' green salt. Gros[2] then obtained a series of light yellow or colourless salts by the action of nitric acid upon the green salt of Magnus. Reiset[3] and Peyronne[4] independently found that by the action of ammonia on Magnus' green salt, or on platinous chloride, two other series of compounds could be obtained. These were distinguished as the chlorides of Reiset's first and second bases. Peyronne showed that Magnus' salt is a platinichloride of the second base. Further investigations of these compounds, and theoretical speculations concerning their constitution, have been made by various other chemists.[5]

These derivatives exist in two series, in which the platinum is divalent and tetravalent respectively.

In the platinous series, the metal is capable of combining with or co-ordinating only 4 molecules or radicles to form the characteristic complex radicle, and the maximum number of external acid radicles is 2, since the platinum is divalent.

In the platinic series, on the other hand, the metal, like chromium, is capable of forming a complex radicle with 6 molecules or radicles, but, platinum being in these salts tetravalent, the maximum number of external acid radicles is 4, instead of 3 as in the derivatives of trivalent chromium.

It is characteristic of the platinum series that the free hydroxides from which the salts are derived are in many cases stable substances, whereas this is rarely the case in the chromium and cobalt series.

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[1] *Pogg. Ann.*, 1828, **14**, 204.

[2] *Ann. Chim. Phys.*, 1838, [2], **69**, 204.

[3] *Ibid.*, 1844, [3], **11**, 417; *Compt. rend.*, 1840, **10**, 870; 1844, **18**, 1103.

[4] *Ibid.*, 1844, [3], **12**, 193; 1846, [3], **16** 462.

[5] Raewsky, *Ann. Chim. Phys.*, 1844, [3], **12**, 278; Gerhardt, *Compt. rend.*, 1850, **31**, 244; Buckton, *Annalen*, 1852, **84**, 220; Thomsen, *Ber.*, 1870, **3**, 42; Odling, *Ber.*, 1870, **3**, 42; Blomstrand, *Ber.*, 1871, **4**, 673; Cleve, *Bull. Soc. chim.*, 1867, [2], **7**, 12; 1871, **15**, 161; **16**, 203; 1872, **17**, 289; Cossa, *Journ. Chem. Soc.*, 1887, **52**, 642; 1896, **70**, ii., 251; *Ber.*, 1890, **23**, 2503; *Zeit. anorg. Chem.*, 1891, **1**, 65; Werner, *ibid.*, 1893, **3**, 267; 1895, **8**, 153; 1896, **12**, 46; see also references given under chromium (p. 1068).

The following are the chief series of these derivatives which have been described, X and R being monovalent acid and basic radicles respectively.

PLATINOUS COMPOUNDS.

1. Tetrammine-platinous compounds, $[(NH_3)_2Pt]X_4$.
   (Plato-diammine.)
2. Triammine-platinous compounds, $[X(NH_3)_3Pt]X$.
3. Diammine-platinous compounds, $[X_2(NH_3)_2Pt]$.
   (Platosammine and platosemidiammine.)
4. Monammine-platinous compounds, $[X_3(NH_3)Pt]R$.
   (Platosemiammine.)

PLATINIC COMPOUNDS.

1. Hexammine-platinic compounds, $[(NH_3)_6Pt]X_4$.
   (Drechsel's base.)
2. Pentammine-platinic compounds; unknown.
3. Tetrammine-platinic compounds, $[X_2(NH_3)_4Pt]X_2$.
   (Platin-diammine.)
4. Triammine-platinic compounds, $[X_3(NH_3)_3Pt]X$.
   (Platinmonodiammine.)
5. Diammine-platinic compounds, $[X_4(NH_3)_2Pt]$.
   (Platinammine and platinsemidiammine.)
6. Monammine-platinic compounds, $[X_5(NH_3)Pt]R$.
   (Platinisemiammine.)

Magnus' Green Salt, $[(NH_3)_4Pt][PtCl_4]$, which is the starting-point for the preparation of these derivatives, is made by the action of ammonia on platinous chloride, and when boiled with ammonia passes into *tetrammine-platinous chloride*, $[(NH_3)_4Pt]Cl_2$.

The tetrammine salts lose ammonia when heated, thus yielding the symmetrical diammine compounds (platosammine salts), whilst the isomeric asymmetrical compounds (platosemidiammine salts) are formed by the moderate action of ammonia on the platinous salts. The platinic salts are formed by the oxidation of the corresponding platinous derivatives. The diammine compounds of both the platinous and platinic series can exist in two geometrically isomeric forms (p. 1092).

In addition to the classes of compounds already mentioned, several others have been described containing organic substituted ammonias in the complex radicle, and also compounds the members of which contain more than one atom of platinum. Little is known of these latter compounds; for a detailed description reference must be made to the original papers.

PLATINUM AND PHOSPHORUS AND ARSENIC.

646 *Platinum and Phosphorus.*—These two elements fuse together readily. If finely divided platinum be heated in the vapour of phosphorus it burns with evolution of light to form *platinum diphosphide*, PtP_2, which is a bright mass with a metallic lustre, not attacked by hydrochloric acid, but easily dissolved by ammonia (Schrötter). According to Granger,[1] the phosphide, Pt_3P_5, is formed at the same time, and this compound is also obtained if platinum be heated at about 600° in phosphorus vapour.

Spongy platinum and arsenic unite with incandescence. The brittle alloy, $PtAs_2$, loses all its arsenic on ignition. Platinum forms brittle alloys also with antimony, bismuth, and vanadium.

PLATINUM AND CARBON.

647 *Platinous Cyanide*, $Pt(CN)_2$, is obtained as a pale yellow precipitate on the addition of mercuric cyanide to an alkali platinochloride solution. It is insoluble in acids and alkalis, and on heating it burns, leaving platinum.

Platinocyanic Acid, $H_2[PtCy_4]$, is obtained by decomposing the copper or mercury salt with sulphuretted hydrogen,[2] or by decomposing the barium salt with dilute sulphuric acid.[3] After evaporating to dryness, the residue is treated with a mixture of alcohol and ether, and the ethereal solution allowed to evaporate spontaneously, when fine cinnabar-red prisms, exhibiting a splendid blue colour by reflected light, are obtained. These have the composition $H_2PtCy_4,5H_2O$. Sometimes yellowish-green crystals, having a copper-red or golden lustre, are obtained which contain more water. When heated to 100° they become yellow, and they decompose at temperatures above 140°. They are deliquescent, yielding a colourless solution in alcohol; the aqueous solution decomposes carbonates.

Potassium Platinocyanide, $K_2PtCy_4,12H_2O$, is formed when a mixture of equal parts of spongy platinum and potassium ferrocyanide is heated nearly to redness in a crucible, the mass dissolved in water, and the filtrate evaporated (Gmelin), or when platinous chloride is dissolved in potassium cyanide.[1] It is also obtained by dissolving ammonium platinichloride together with caustic potash in a boiling concentrated solution of potassium cyanide. The liquid is boiled until no further evolution of ammonia takes place, when the salt crystallises out.[2] This is also formed when spongy platinum is boiled with a solution of potassium cyanide, or when a mixture of these two substances is heated at 500° to 600° in steam (Deville and Debray):

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[1] *Compt. rend.*, 1896, 123, 1284.

[2] Quadrat, *Annalen*, 1847, 63, 164; 1848, 65, 249; 1849, 70, 300.

[3] Weselsky, *J. pr. Chem.*, 1856, 69, 276.

$$4KCy + Pt + 2H_2O = K_2PtCy_4 + 2KOH + H_2.$$

It forms long, yellow, rhombic prisms, exhibiting a blue, metallic lustre by reflected light, and it is very readily soluble in water. If the hot solution be saturated with chlorine, or boiled with aqua regia, colourless prisms of *potassium chloroplatinicyanide*, $K_2PtCy_4Cl_2,2H_2O$, are obtained on evaporation. If this solution be mixed in the right proportion with potassium platinocyanide a double salt of the composition $5K_2PtCy_4,K_2PtCy_4Cl_2,21H_2O$ is obtained crystallising in magnificent green prisms which exhibit a copper-red lustre by reflected light and are soluble in water. This salt is formed also when potassum platinocyanide is treated with a moderate quantity of chlorine.[3] In alkaline solution it acts as an oxidising agent, potassium hypochlorite being formed:

$$5K_2PtCy_4,K_2PtCy_4Cl_2 + 2KOH = 6K_2PtCy_4 + KOCl + KCl + H_2O.$$

Barium Platinocyanide, $BaPtCy_4,4H_2O$, was first obtained by passing hydrocyanic acid into water containing platinous chloride and barium carbonate in suspension.[4] It can also be readily obtained by decomposing the copper salt by baryta water, or by adding the calculated quantity of barium hydroxide and hydrocyanic acid to a solution of platinichloric acid, and treating the warm mixture with sulphur dioxide until colourless. The barium sulphate formed is filtered off and the solution cooled, when barium platinocyanide separates out and may be purified by recrystallisation from water. This method of preparation serves as a means of separating platinum from iridium, the compound of the latter metal remaining in solution.[1] Barium platinocyanide forms large, rhombic crystals which exhibit a green and sulphur-yellow dichroism. By crystallising the salt from solution in the presence of a small quantity of barium cyanide or barium hydroxide Levy[2] obtained apple-green crystals, whilst in the presence of a small amount of hydrogen cyanide or other acids golden-yellow crystals were produced. The crystals also differed in their fluorescent properties and slightly in density, but their crystalline form was identical. Levy regards the two forms as isomers differing in the manner in which the water molecules are grouped, but it is possible that the differences in properties may be accounted for by the presence of traces of other salts. Barium platinocyanide has also been obtained as the dihydrate and as the anhydrous salt.

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[1] Knop, *Annalen*, 1842, 43, 111.

[2] Martius, *Annalen*, 1861, 117, 357.

[3] Hadow, *Journ. Chem. Soc.*, 1861, 13, 106.

[4] Weselsky, *J. pr. Chem.*, 1856, 69, 276.

Calcium Platinocyanide, $CaPtCy_4,5H_2O$, is prepared in the same way as the barium salt. Two isomers have been similarly obtained,[2] yellow and green in colour but of indentical crystalline form. The anhydrous salt is white.

Magnesium Platinocyanide, $2MgPtCy_4,7H_2O$, is obtained by decomposing the barium salt with magnesium sulphate, and is one of the most beautiful salts of this group. It forms large, square-based, red prisms, the sides of which viewed by reflected light have a beetle-green lustre, whilst the end faces reflect blue or purple light. It crystallises from alcohol with six molecules of water in four-sided, lemon-yellow tablets, having a blue reflection, and often exhibiting all shades of colour of red, blue, and green. Other hydrates are also known.

Many other platinocyanides besides these are known, of which several are remarkable for their splendid play of colours. Some, such as the green copper salt, are insoluble powders obtained as precipitates by double decomposition. A very characteristic reaction for the platinocyanides is that on addition of a mercurous or a mercuric salt to their solution a white precipitate is first thrown down, but on addition of more mercurous salt this becomes of a smalt-blue colour.

These salts become luminous when exposed to the Röntgen rays, and are employed for making screens by means of which the absorption of these rays may be observed.

Platinum Tricyanide, $PtCy_3$, is obtained as a light yellow powder on heating platinicyanic acid to 120°. It is insoluble in water but dissolves in a boiling solution of potassium cyanide.[1]

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[1] Bergsöe, *Zeit. anorg. Chem.*, 1899, 19, 318.

[2] *J. Chem. Soc.*, 1908, 93, 1446; *ibid.*, 1912, 101, 1081; Levy and Sisson, *ibid.*, 1906, 89, 125.

Platinicyanic Acid, $HPtCy_4$, is obtained by evaporating a fairly concentrated solution of platinocyanic acid with hydrogen peroxide on the water-bath:[1]

$$2H_2PtCy_4 + H_2O_2 = 2HPtCy_4 + 2H_2O.$$

As evaporation proceeds the white substance at first formed turns pink, brown, and finally dull olive-green. This is platinicyanic acid, $HPtCy_4,2H_2O$. The colour changes are due to differences in the degree of hydration and take place in the reverse order when water is added to the acid.

The acid is reduced to platinocyanic acid on boiling with sulphur dioxide, and liberates iodine from potassium iodide solution quantitatively according to the equation:

$$2HPtCy_4 + 2KI = 2KHPtCy_4 + I_2.$$

Silver Platinicyanide, $AgPtCy_4$, is obtained as a brown, flocculent precipitate on the addition of silver nitrate to a solution of platinicyanic acid. When dry it is a buff-coloured powder which on ignition leaves a residue of silver and platinum.

Oxidation of the platinocyanides with hydrogen peroxide in sulphuric acid solution yields the corresponding platinicyanides. With strong solutions, the pure *sodium* and *lithium* salts have been obtained. More usually, however, compounds of the platinicyanides with the platinocyanides are produced, as, for example, $LiPtCy_4,2Li_2PtCy_4$, and $KPtCy_4,3K_2PtCy_4$.[1]

Potassium Platinothiocyanate, $K_2Pt(SCN)_4$, is obtained by dissolving platinum dichloride in a solution of potassium thiocyanate, or, better, by dissolving equal parts of potassium platinochloride and potassium thiocyanate in the smallest quantity of water, when the mixture becomes warm, and, on cooling, the salt separates out in red, microscopic prisms. When the barium salt is decomposed by dilute sulphuric acid, the free acid is obtained in solution, but undergoes rapid decomposition.[2]

Platinithiocyanic Acid, $H_2[Pt(SCN)_6]$.—On decomposing the lead salt with dilute sulphuric acid, a thick, dark red, very acid liquid is obtained, which decomposes carbonates, and dissolves zinc with evolution of hydrogen. On evaporation in a vacuum, an indistinct, crystalline mass remains behind.

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[1] Levy, *Journ. Chem. Soc.*, 1912, **101** 1081.

[2] Buckton, *Journ. Chem. Soc.*, 1855, 22.

Potassium Platinithiocyanate, $K_2Pt(SCN)_6$, is obtained by adding potassium thiocyanate solution, not in excess, to a solution of potassium platinichloride and heating to boiling. The filtered solution on cooling deposits large, six-sided prisms or tablets having a carmine-red colour and possessing a very disagreeable taste. They dissolve in water, forming such a deep red solution that one drop of the concentrated liquid imparts a distinct colour to 100,000 parts of water. When the concentrated solution is boiled with ammonium sulphate a very similar ammonium platinithiocyanate is formed. The platinithiocyanates of the alkali metals are soluble in water and crystallisable; those of the heavy metals are insoluble, and have a yellowish- or blackish-red colour (Buckton).

DETECTION AND ESTIMATION OF PLATINUM.

648 If a platinum compound be heated on a carbonised match in the gas-flame, a grey, spongy mass is obtained soluble only in aqua regia. The concentrated solution yields with potassium chloride and ammonium chloride the well-known and characteristic precipitates. Sulphuretted hydrogen throws down from solutions of a platinum salt, slowly in the cold but more quickly on heating, the brown disulphide which is soluble in an excess of yellow ammonium sulphide. A solution of stannous chloride colours platinic chloride solutions dark brown, inasmuch as platinous chloride is formed. A solution of benzidine in acetic acid forms a delicate reagent for the detection of platinum, a blue, flocculent precipitate being obtained. Iron and gold also give blue colorations with this solution.[1]

In the general separation of the metals, platinum and gold are obtained together with arsenic, antimony, and tin. Their presence is indicated by the brown colour of the precipitate produced by hydrochloric acid in the solution in ammonium sulphide. In this case the precipitate is fused with sodium carbonate and nitre, the fused mass lixiviated with water, and the residue, which may contain the gold and platinum together with tin dioxide and sodium antimonate, is treated with zinc and hydrochloric acid when the latter two compounds are reduced to metals. The mass is first boiled with hydrochloric acid to remove the tin, and next with nitric acid and a little tartaric acid to dissolve the antimony; the residue is then treated with aqua regia, the solution concentrated and evaporated to dryness on the water-bath with an excess of ammonium chloride, and alcohol added to dissolve the gold chloride. From the alcoholic solution the gold may be readily precipitated with ferrous sulphate. The portion insoluble in alcohol may contain ammonium platinichloride, and this on ignition will leave a residue of spongy platinum. The qualitative separation of the platinum metals by means of their sulphides has already been described (p. 1437).

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[1] Malatesta and Di Nola, *Boll. Chim. Farm.*, 1913, 52, 461.

An alternative method for the rapid qualitative analysis of a mixture containing these metals has been devised by Mylius and Dietz.[1] A solution of the chlorides is boiled in a retort with dilute nitric acid and the vapours passed into a solution of caustic soda. If osmium be present it is thus converted into the volatile tetroxide which forms a yellow solution in the soda and may be detected in the usual manner. The residual liquor, after extraction with ether to remove gold chloride, is then heated with ammonium acetate and formic acid for several hours in a reflux apparatus, whereby the salts of the platinum metals are reduced to the metals, and the black precipitate, after washing and drying, is heated to redness in a stream of hydrogen to remove mercury. The residue is then extracted with hydrochloric acid, mixed with sodium chloride, heated in chlorine, and the product dissolved in a little water, filtered, and ammonium chloride added so long as any precipitate forms. In this way the platinum, iridium, and ruthenium are precipitated, whilst the palladium and rhodium remain in solution, but the separation is not quantitative. The precipitate is dissolved in warm water, treated with hydroxylamine, and again precipitated with ammonium chloride, whereby the tetrachlorides of ruthenium and iridium first formed are converted into the trichlorides which remain in solution, whilst the platinum is precipitated as ammonium platinichloride. Ruthenium and iridium are separated in the filtrate from this precipitate by evaporating to dryness, reducing to the metals in a current of hydrogen, fusing with potash and nitre, extracting with water, and distilling off the volatile ruthenium tetroxide in a current of chlorine into dilute acidified alcohol. The iridium is detected in the insoluble residue by treatment with chlorine and sodium chloride and precipitation with ammonium chloride. The original filtrate containing rhodium and palladium is evaporated

[1] *Ber.*, 1898, 31, 3191.

to dryness with excess of ammonia, the residue dissolved in the least possible quantity of ammonia and cooled, when the less soluble ammoniacal rhodium chloride separates out, and the palladium may be precipitated from the filtrate by hydrochloric acid as palladosammine chloride.

The *quantitative estimation* of platinum always takes place as metal, obtained by ignition of ammonium platinichloride, or by heating potassium platinichloride in a current of hydrogen and lixiviating the residue with water, or sometimes also by ignition of the sulphide.

The Atomic Weight of platinum was determined by Berzelius[1] by analysis of the potassium double chloride; the mean number obtained by him was 197·1; Andrews,[2] who employed the same method, found the atomic weight to be 197·9, but Seubert[3] obtained 195·14, and Halberstadt,[4] confirming this result, found 195·07. More recent work by Archibald,[5] who analysed the carefully purified potassium and ammonium salts of chloro- and bromo-platinic acids, has given as a mean of twenty-eight determinations the figure 195·23. The value now (1922) adopted is 195·2.

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[1] *Lehrbuch*, 5te *Aufl.* 3, 1212.

[2] *Chem. Gaz.*, 1852, 379.

[3] *Annalen*, 1881, **207**, 1.

[4] *Ber.*, 1884, **17**, 2963.

[5] *Proc. Roy. Soc. Edin.*, 1909, **29**, 721.

THE RADIOACTIVE ELEMENTS.

649 Becquerel's discovery of the radioactivity of uranium in 1896 has led to the development of an entirely new branch of scientific thought. Special methods of investigation, mainly physical in character, have been invented, and the results are of extraordinary interest and importance. Much, however, yet remains to be done before many of the conclusions hitherto drawn can be considered as established, and discoveries are constantly being made. In these circumstances only a very brief outline of the subject is here attempted.[1]

650 The phenomena of the electrical discharge in an ordinary vacuum tube containing gas at a few millimetres pressure are quite familiar. If the tube contain air or nitrogen, the negative pole, or cathode, is clothed with a violet glow, quite distinct from the brick-red positive column, which occupies most of the tube. The narrow portion of the tube may be bent into any curved form—a spiral, for example—and the discharge follows all the curves. But the phenomena are quite different if the vacuum in the tube be greatly increased; the dark space separating the cathode from the violet glow becomes much greater, and the discharge from the cathode refuses to follow the curves of the tube, but pursues a straight course, normal to the surface of the cathode, until it strikes the glass, where it produces phosphorescence. The phenomena of such high vacua were investigated by Crookes[2] in 1870. He found these electric streams from the cathode produced brilliant phosphorescence in diamonds, rubies, etc., and threw well-defined shadows of objects placed in their path upon the opposite wall of the tube, which phosphoresces all round the shadow. Further, this electric stream can put lightly poised vanes into motion, and it is deflected by a magnet brought near the tube. Such an electric stream is now spoken of as consisting of "cathode rays." It was shown by Hertz that

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[1] A full account of the subject is given in *Radioactive Substances and their Radiations*, by Rutherford (Cambridge: The University Press, 1913). The chemical behaviour of radioactive bodies is dealt with by Soddy in *The Chemistry of the Radio-Elements* (Longmans).

[2] *Phil. Trans.*, 1874, 164, 501; 1875, 165, 519; 1876, 166, 325.

the cathode rays, though they will not pass through glass or mica, will penetrate thin metal foil, and Lenard, by constructing vacuum tubes with aluminium "windows," observed the cathode rays to pass out through the metal into the air, there to produce phosphorescence, although the rays cannot be produced at all in air at ordinary pressure. Crookes aptly spoke of these phenomena as belonging to a "fourth state" of matter, quite different from matter in either the solid, liquid, or gaseous state. The cathode rays are now recognised as streams of electrons carrying negative charges.

J. J. Thomson showed,[1] in 1897, that the cathode rays are not only deflected in a magnetic field, but also by an electric field, and this is what should occur if the rays are streams of negatively electrified particles. He employed a vacuum tube so arranged that the cathode stream passed midway between two parallel insulated plates of metal, respectively charged positively and negatively. When the plates were uncharged the cathode stream produced a luminous spot on the end of the tube, but when the plates were charged the displacement of this spot showed that the stream had been deflected towards the positively charged plate, thus proving that the particles of the stream carried a negative charge. By means of an electro-magnet the stream could be deflected in the opposite direction so as to bring the spot back to its original position. By measuring the strengths of the electric and magnetic fields, data were obtained for calculating the velocity of the particles, and also the ratio of the electric charge to the apparent mass of a particle. The strength X of the electric field is V/d, where V is the difference of potential between the plates and d their distance apart. If H be the strength of the magnetic field, the force acting on a particle with charge e and moving with velocity u is Heu, and at equilibrium,

$$Heu = Xe \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If the magnetic field be acting alone, a particle of mass m and charge e describes a circular orbit of radius ρ, such that:

$$\mathrm{H}\rho = \frac{mu}{e} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From equations (1) and (2) the values of u and e/m can be determined. By measurements made in this way it has been found that the velocity of the particles varies between about 10^9

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[1] *Phil. Mag.*, 1897, [5], 44, 293.

and 10^{10} cm. per second. (The velocity of light is 3×10^{10}, and the velocity of the molecules of hydrogen in the gas at N.T.P. $1{\cdot}844 \times 10^5$ cm. per sec.) These experiments do not, however, give us the mass of a particle, but only the ratio of the charge to the mass. It follows from Faraday's laws of electrolysis that all monovalent ions in electrolysis carry the same charge, and experiment has shown that it requires $9{\cdot}6 \times 10^3$ electromagnetic units of electricity to set free one gram of hydrogen. If N be the number of atoms in one gram of hydrogen, then $Ne = 9{\cdot}6 \times 10^3$, and if m be the mass of a hydrogen atom, then $Nm = 1$. Hence $e/m = 9{\cdot}6 \times 10^3$ for the hydrogen ion. Simon[1] obtained an average value of $1{\cdot}86 \times 10^7$ (with an average velocity of 7×10^9) for the ratio e/m for the cathode rays, and if we assume that the charge of the particles (or electrons) is the same as that of an atom of hydrogen, so that e has the same value in the two equations $e/m = 1{\cdot}86 \times 10^7$ and $e/m' = 9{\cdot}6 \times 10^3$ (where m' is the mass of the hydrogen atom), then $m' = 1943m$. The mass of the particle in the cathode rays is thus about the one two-thousandth part of the mass of a hydrogen atom. According to the work of Millikan the value is 1/1830 of the mass of a hydrogen atom (see p. 40).

It has been mentioned that the cathode rays excite phosphorescence in the glass of the tube at the place where they impinge, or in other substances placed in the path of the stream of electric particles. In 1895 Röntgen discovered that in these circumstances the phosphorescent glass emitted rays of a most remarkable character—the so called X-rays—capable of penetrating such opaque substances as paper, wood, aluminium, flesh, etc., but stopped by lead, platinum, glass, or bone. These rays have the power of exciting fluorescence in such substances as barium platinocyanide, and of affecting a photographic plate; so that it is possible to photograph, or by the use of a fluorescent screen to see, the shadow of the bones of the hand, or a coin concealed between the pages of a book. The X-rays are incapable of refraction or reflection from isotropic media; recently, however, reflections have been obtained from crystalline substances such as mica, but this phenomenon is more analogous to interference in optics than to true reflection[2] (p. 216). The rays are not sensibly acted on by a magnet. They have been found to have the power of discharging an electroscope.

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[1] *Ann. Physik*, 1899, 69, 589.

[2] Laue, Friedrichs, and Knipping, *Sitzungsber. Bayr. Akad. Wiss.*, 1912, 303.

There is another type of ray which is observed when an electric discharge passes through a rarefied gas. It was shown by Goldstein[1] that under certain conditions of pressure streams of rays pass through the holes in a perforated cathode. These streams are known as canal rays, and have been shown by Wien to consist of positively charged particles moving with high velocities. From measurements of their deflection in electric and magnetic fields, it appears that the carriers of the electricity are of atomic size and thus differ in this respect from the cathode particles, as well as in carrying electricity of opposite sign. This distinction between the sizes of the carriers of positive and negative electricity is general and of great importance, and will be seen later to exist in the positively and negatively charged radiations emitted by radioactive bodies.

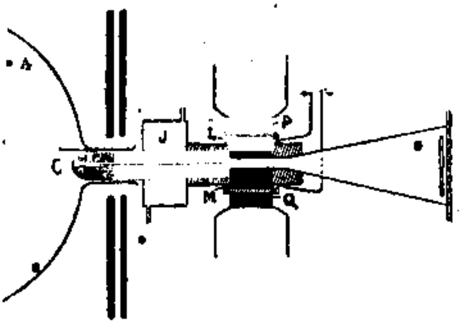

FIG. 205.

651. Some experiments by J. J. Thomson[2] are of particular interest as a delicate means of chemical analysis. The method consists in subjecting the positive rays simultaneously to an electric and a magnetic field and noting the deflection suffered by the rays. The electric and magnetic fields are arranged to be in the same direction so as to deflect the rays in two directions at right angles to each other, with the result that the particles move along different paths determined by the masses and velocities of the particles. The experimental arrangement will be understood from Fig. 205. An electric discharge is passed through the rarefied gas contained in the vessel, A, provided with a cathode, C, with a small hole at its

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[1] *Berlin Sitzungsber.*, 1886, 39, 691.

[2] J. J. Thomson, *Rays of Positive Electricity*.

centre. The positively electrified particles which move with great velocity towards the cathode pass through this hole and emerge as a fine pencil of electrified particles passing between the plates, L and M, connected to the positive and negative poles of a battery, and between the pole-pieces, P and Q, of an electromagnet. The heterogeneous pencil of particles, all of which follow the same course before entering the electric and magnetic fields, is split up into a number of groups of rays branching off in different directions. No two particles move along the same path unless they have the same masses and also the same velocities. It can be shown that all particles with the same masses but with different velocities move along the surface of a cone which is peculiar to the particular particle, so that if this cone is determined, the nature of the particle carrying the positive charge is also known; in this way, from a study of the path traversed by a particle, it is possible to deduce its mass and therefore the chemical nature of the atom or molecule constituting the positive radiation. The cones are determined by observing their parabolic sections on a photographic plate placed in the path of the rays. A typical photograph obtained in this way is shown in Fig. 206. The photograph was obtained with the

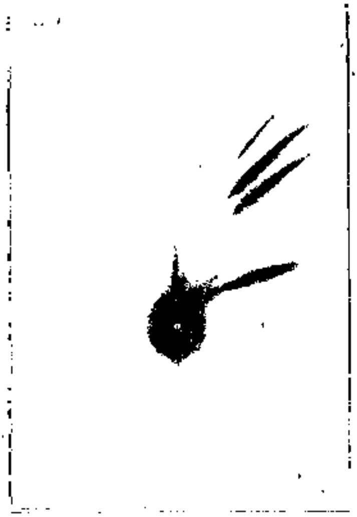

FIG. 206.

residues from liquid air containing the lighter gases; there are present lines corresponding to helium, neon, argon, and also a line of special interest corresponding to an atomic weight 22, which could not be identified with the line of any known gas; for the possibility of its being due to molecules of CO_2 carrying a double charge of electricity is precluded by the fact that on passing the gases through tubes immersed in liquid air the line persisted, whereas the line at 44, due to carbon dioxide, disappeared. There seems to be no doubt that the line is due to a new gas of atomic weight 22 contained in the atmosphere and closely associated in properties with neon; for it is found in all the specimens of neon which have been examined.

The nature of the positive rays is very complicated, since the particles constituting them may consist either of atoms or molecules, with single or multiple changes. The method of examination described above is hardly capable of disentangling their complexities, but a modification and refinement devised by Aston[1] has given results of striking importance. The improvement consists in so arranging the apparatus that after deflection by an electric and a magnetic field, rays having the same value of $\frac{e}{m}$ are brought approximately to a focus on a photographic plate, and in this way a "positive ray spectrum" or "mass spectrum" of the radiation is obtained. The general arrangement adopted is shown in Fig. 207. The rays after

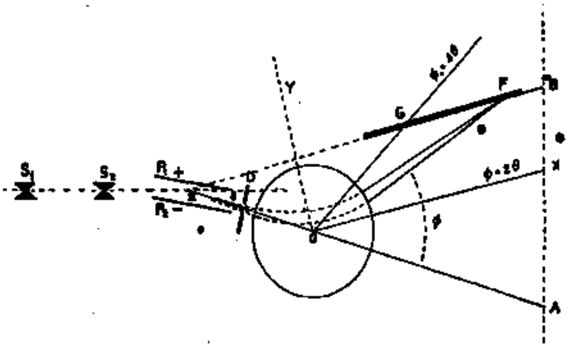

FIG. 207.

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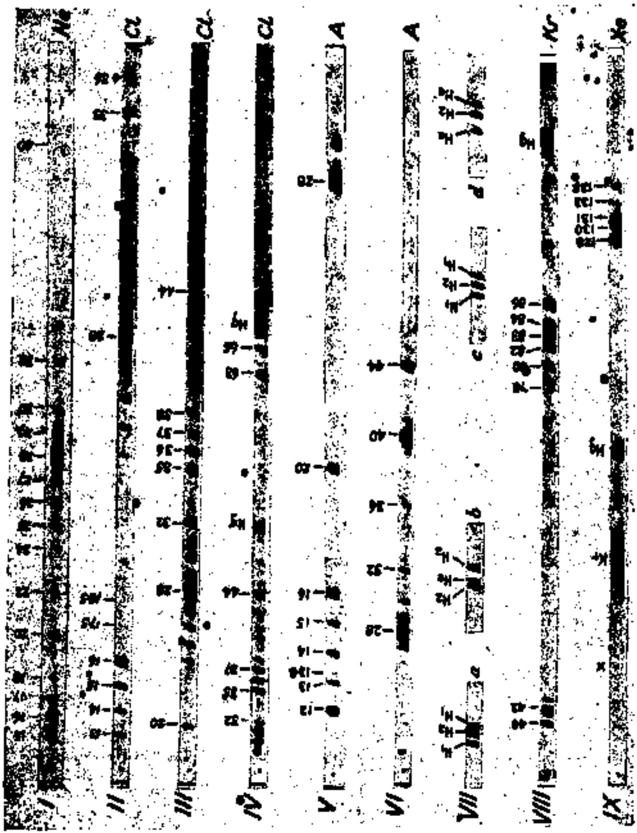
[1] Aston, *Phil. Mag.*, 1919, [6], **38**, 707; 1920, [6], **39**, 449, 611; 1920, [6], **40**, 628; 1921, [6], **42**, 140, 436. Aston and Fowler, *ibid.*, 1922, [6], **43**, 514.

reaching the cathode pass through two narrow parallel slits S_1, S_2, and the resulting beam passes between the parallel plates P_1, P_2, maintained at different electric potentials. The rays deflected by the electric field may be considered to diverge approximately from a point, Z, at the middle of the field. A group of these rays passes through the diaphragm, D, and into a magnetic field maintained by an electro-magnet with circular pole-pieces. The magnetic field is arranged to deflect the beam in a direction opposite to that produced by the electric field. It can be shown that with this method rays having various values of $\frac{e}{m}$ will all be brought to a focus on a photographic plate, GF.

Typical photographs taken with the positive ray spectrograph are shown in Fig. 208. The various spectrographs shown are indicated as belonging to different elements Ne, Cl, A, Kr, Xe, etc.; but it must be realised that with this delicate method of analysis it is impossible to exclude impurities arising from gases occluded in the walls of the tube and from hydrocarbons emitted by the tap grease unavoidably used in the apparatus. A very careful study of each spectrograph is therefore necessary before the disturbances arising from impurities can be eliminated. Lines due to elements will appear for values of $\frac{e}{m}$ corresponding with the atomic weights of the elements, and with single, double, and treble charges. Following a nomenclature, analogous to that of optics, lines due to singly-charged atoms are known as first order spectra, those due to doubly-charged atoms as second order spectra, and so on. The complication arising from charged molecules is fortunately rendered less serious by the fact that in most cases molecular spectra appear only in the first order. The large number of lines in the spectrographs (Fig. 208) arising from hydrocarbons and other carbon compounds can thus be identified and left out of consideration. For measurement, it is necessary to establish certain standard lines; oxygen gives a useful set of lines for this purpose, showing, as it does, lines at 32, 16, and 8, due, respectively, to the singly-charged molecule and to the singly- and doubly-charged atoms. Other useful lines of reference are found at $C^{++}(6)$, $C^{+}(12)$, $CO^{+}(28)$ and $CO_2^{+}(44)$. By comparison with these and other lines, the masses corresponding with any particular lines can be accurately determined.

It is not proposed to enter into a full discussion of the complicated results shown in Fig. 208, for a single example, that of chlorine, will suffice to indicate the manner in which the results have been interpreted.

Spectrum 1 shows two lines at 20 and 22 due to neon found by J. J. Thomson as mentioned above. On introducing phosgene ($COCl_2$) into the tube the spectra shown in II, III, and IV were obtained. It will be seen that the introduction of chlorine has produced a series of lines at 35, 36, 37, and 38, but no line appears in the position corresponding with the accepted atomic weight, 35·46. On spectrum II may be seen lines at 17·5 and 18·5 when free chlorine was introduced and lines corresponding with 35



and 37. The lines at 36 and 38 are ascribed by Aston to hydrochloric acid formed from chlorine of atomic weights 35 and 37 respectively.

We thus have two examples of elements, neon and chlorine each appearing to have two distinct atomic weights represented by whole numbers, 20 and 22 in the case of neon, and for chlorine 35 and 37. Similar results have been found with other elements, and it is impossible to escape from the conclusion that we can no longer regard the elements as made up of exactly similar atoms, but, on the other hand, that they consist of a mixture of atoms having integral atomic weights mixed in different proportions. These atoms, however, are inseparable by any chemical process, being in every way identical in chemical properties. The only means of separating them is by some method, such as that of mass spectra, depending for its action on the masses of the constituents. Such atoms having identical chemical properties but different masses are known as *isotopes* (see p. 74), since they occupy the *same place* in the periodic table. Elements with different chemical properties but the same atomic weights are known as *isobares*. The further point that the constituent isotopes of any element are whole numbers is of great importance, and will be considered later. Evidence as to the existence of isotopes was first obtained by a study of the radioactive elements (p. 74). Some typical results obtained by Aston are given in the table on p. 1499.

The atomic number is the numerical position of the element in the periodic system of elements (p. 72).

652 In 1896, Becquerel[1] found that uranium potassium sulphate crystals were able to affect a photographic plate wrapped up in black paper. The effect was produced also through thin glass or metal, and both by uranium metal itself and by all its compounds, either in the solid state or in solution. The activity of a uranium salt enclosed in a thick lead box, and never exposed to light, was observed by Becquerel to continue undiminished for four years, and was not affected by variations of temperature from 200° to that of liquid air. He also observed that the rays from uranium, which are known as Becquerel rays, have the power of discharging an electroscope, whether positively or negatively charged. They are similar in these respects to the *X*-rays, but their action is feeble in comparison, since it requires several days' exposure to produce a marked action on a

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[1] *Compt. rend.*, 1896, **122**, 188, 233, 356, 452.

Element.	Atomic number.	Atomic weight.	Minimum number of isotopes.	Masses of isotopes in order of intensity.
H	1	1·008	1	1·008
He	2	3·99	1	4
Li	3	6·94	2	7, 6
B	5	10·9	2	11, 10
C	6	12·00	1	12
N	7	14·01	1	14
O	8	16·00	1	16
F	9	19·00	1	19
Ne	10	20·20	2	20, 22 (21)
Na	11	23·0	1	23
Al	13	27·0	1	27
Si	14	28·3	2	28, 29, (30)
P	15	31·04	1	31
S	16	32·06	1	32
Cl	17	35·46	2	35, 37
A	18	39·88	(2)	40 (36)
K	19	39·1	2	39, 41
Fe	26	55·84	1	55·94 ± 0·05 (54)
As	33	74·96	1	75
Se	34	79·2	6	80, 78, 76, 82, 77, 74
Br	35	79·92	2	79, 81
Kr	36	82·92	6	84, 86, 82, 83, 80, 78
Rb	37	85·45	2	85, 87
Sn	51	118·7	8	120, 118, 116, 124, 119, 117, 122, 121
Sb	52	120·2	2	121, 123
I	53	126·92	1	127
Xe	54	130·2	7	129, 132, 131, 134, 136, 128, 130
Cs	55	132·81	1	133
Hg	80	200·6	(6)	(197–200), 202, 204

photographic plate with the Becquerel rays, whereas with the *X*-rays a photograph can be taken in less than a minute.

Becquerel's discovery was followed in 1898 by the observation made independently by Schmidt[1] and Mme. Curie,[2] that the compounds of thorium and minerals containing this element also emit radiations of a similar character to the Becquerel rays. These discoveries have led to the recognition of an entirely new class of substances which possess the remarkable property of radioactivity.

Radioactive substances spontaneously emit rays possessing in varying degrees the properties of canal, cathode, and *X*-rays. The phenomena available for the study of the radiations from such substances are :

(*a*) The action on a photographic plate.

(*b*) The phosphorescence produced in certain substances : *e.g.*, the platinocyanides, willemite (zinc silicate), kunzite, and Sidot's blende (crystalline zinc sulphide).

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[1] *Ann. Physik*, 1898, 65, 141.

[2] *Compt. rend.*, 1898, 126, 1101.

(c) The ionisation of gases produced by the rays.

The last of these lends itself most readily to quantitative measurements, and is generally employed for measuring the degree of radioactivity possessed by a substance.

According to the theory of the ionisation of gases of J. J. Thomson and Rutherford,[1] this effect is due to the production of ions or positively and negatively charged carriers in the gas, the rate of production being proportional to the intensity of the radiation. These ions move with uniform velocity through a uniform electric field, the positively charged towards the negative plate, and *vice versâ*, and their velocity is proportional to the strength of the field. The separated ions gradually recombine, the rate of recombination being proportional to the square of the number present. An ionised gas preserves its conducting power for some time after removal of the ionising agent, and may be carried in a current of air so as to discharge an electroscope some distance away.

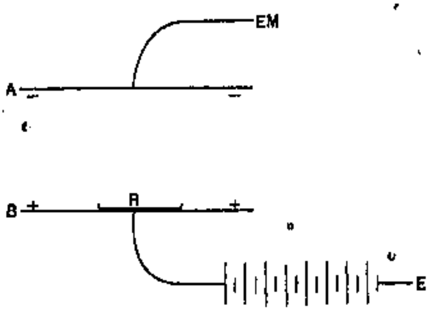

FIG. 209.

The arrangement for measuring the rate of ionisation produced by *X*-rays or cathode rays or by the presence of radioactive material is shown diagrammatically in Fig. 209.

The active material is placed at R on the lower of two insulated plates, A and B, charged respectively negatively and positively by means of a battery connected to B and with the other pole earthed at E. The plate A is connected to one pair of quadrants of an electrometer, EM, of which the other pair is earthed. The gas between the plates A and B being ionised at a constant rate if no electric field be present, the number of ions soon reaches a maximum, when the rate of production of fresh ions is balanced by the rate of recombination. If, however, B be kept charged to a constant potential V, the rate at which the plate A gains charge may be measured by the quadrant electrometer, EM. Positive ions travel to the negative plate A, and negative ions to the positive plate B; there is thus a current through the gas which is measured by the rate at which A rises in potential.

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[1] *Phil. Mag.*, 1896, [5], 42, 392.

When V is small the current is small, but as V increases the current rapidly rises to a limit and then remains constant even when the value of V is largely increased. This condition is not always attainable in practice, a slight increase of current generally occurring with increase of V. This limiting *saturation current* through the gas thus measures the charge carried by the ions produced per second by the radiation, that is, it is a measure of the radioactivity of the substance under examination. For uranium, and for substances not more than a thousand times as active as uranium, a potential difference of 300 volts is usually sufficient, but for radium, and for very active substances, the plates are placed close together, and a higher voltage may be necessary.

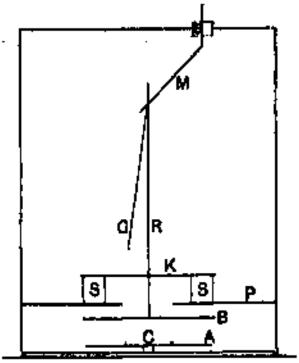

Fig. 210.

Frequently, some form of gold-leaf electroscope is used to measure the saturation current. Such an electroscope is shown in Fig. 210. A strip of gold-leaf, G, is attached to a vertical rod, R, which is supported by the horizontal rod K, resting on sulphur, SS, by which the system is insulated. The rod R passes through an opening in the metal plate P, and terminates in a horizontal plate, B, which is opposed to the removable plate A, on which the radioactive material, C, is placed. The whole is enclosed in a metal case and the motion of the gold-leaf is observed through an opening in the metal case by means of a microscope of low power provided with a micrometer eyepiece. M is a bent wire passing through an insulating plug of sulphur, S, in the top of the case; by means of this wire the electroscope can be charged. During an observation the metal case and the lower plate A are connected to earth, and the time taken for the gold-leaf to pass over a fixed part of the scale is determined, this observation being corrected for the "natural leak" of the instrument, measured when no radioactive material is present. The measurements are generally comparative, uranium oxide being often used as a standard of comparison. The instrument described above is typical of an electroscope used for such measurements. The details of construction will depend upon the particular measurement to be made.[1]

In the examination of radioactive substances, and in the search for new radioactive material, the electroscope has proved an invaluable guide. Bunsen showed that 0·0000003 milligram of sodium could be detected by spectrum analysis; but for the detection of substances like radium the electroscope is many thousand times as sensitive as the method of spectrum analysis, for by its means a substance having only the ten-thousandth of the activity of uranium can be detected; the activity of radium is about 2,000,000 times that of uranium.

PHENOMENA OF RADIOACTIVITY.

653 The radiations from radium and most of the radioactive substances are found to be complex. The different kinds of radiation are distinguished by their different behaviours in a magnetic field and by their different powers of penetrating metal screens, etc. By these methods it has been found that radium emits three different kinds of rays, which have been called by Rutherford α-, β-, and γ-rays respectively.

The α-rays are analogous to canal rays and are easily absorbed by thin metal foil and by a short column of air. Their deflection in a magnetic field is slight compared with that of the β-rays, but is in the opposite direction, proving that they are positively charged. The magnitude of their deflection shows that they are moving with a velocity approximately one-tenth of that of light.

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[1] See Makower and Geiger, *Practical Measurements in Radioactivity* (Longmans, 1912).

The β-rays are identical with the cathode rays produced in a highly exhausted vacuum tube: they are deflected by a magnetic field in such a direction as to show that they are carriers of negative electricity. They are completely absorbed by one millimetre of lead. Their velocity is, however, much greater than that of the cathode rays in a vacuum tube, the β-rays from radium varying in velocity between about 10^{10} and nearly 3×10^{10} cm. per second. Their penetrating power increases rapidly with the velocity, and some of those expelled from radium penetrate a thickness of a millimetre of lead.

Besides the α- and β-rays, uranium, thorium, and radium compounds emit very penetrating rays known as γ-rays, the penetrating power of which is 100 times that of the β-rays, so that the rays can be detected after passing through several centimetres of lead. These rays are not deflected[1] in a magnetic field. They can easily be detected from a few milligrams of radium bromide enclosed in a lead vessel of 1 cm. thickness (which completely absorbs the α- and β-rays) by the luminosity they produce in a fluorescent screen of barium platinocyanide or of willemite, when observed in a dark room. The γ-rays, which are similar in nature to X-rays, are usually associated with β-rays, and are probably produced in some way from the β-particles as they escape from the atom. It has, however, been shown by Chadwick[2] that γ-rays may be produced in small quantity from α-rays.

The different behaviours of the three kinds of rays in a magnetic field is diagrammatically illustrated[3] in Fig. 211.

R represents the radium compound placed at the bottom of a small cylindrical lead vessel, standing on a photographic plate, AC. By a strong magnetic field applied at right angles to the plane of the paper and directed towards the paper, the three types of radiation are separated: the γ-rays take a straight course without being deflected by the field, the β-rays are deflected to the right, describing circular paths, and affect the photographic plate on the right of R, while the α-rays are slightly deflected to the left, but are quickly absorbed by the air.

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[1] Villard, *Compt. rend.*, 1900, **130**, 1010, 1178; Becquerel, *ibid.*, 1154.

[2] *Phil. Mag.*, 1913, [6], **25**, 193.

[3] Rutherford, *Radioactive Substances*, p. 116.

The phosphorescence produced in a zinc sulphide screen by radium is chiefly due to the α-rays. This phenomenon was discovered by Crookes,[1] and is well exhibited by his apparatus, known as the *spinthariscope*. In this a fine metallic point, which has been dipped in a solution of a radium salt, is fixed a millimetre or two above a zinc sulphide screen, which is examined with a magnifying glass in darkness. The surface of the screen is then seen to be dotted with flashes of light, which follow each other rapidly, and this action is kept up without any apparent diminution for years. It has been shown that nearly every α-particle striking the screen produces a flash of light, and this property has been employed to count the number of α-particles emitted by a source of radiation.[2]

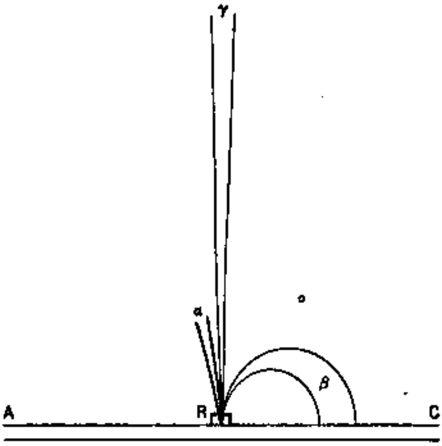

FIG. 211.

The velocity of the α-ray is not easy to determine exactly, because of the smallness of the deflection of the α-particles in an electric or a magnetic field. Rutherford and Robinson[3] have found it to be $1{\cdot}92 \times 10^9$ cm. per second, whilst the ratio $e/m = 4{\cdot}82 \times 10^3$ E.M. units. This value of e/m is almost exactly half that of the hydrogen ion in electrolysis.

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[1] *Proc. Roy. Soc.*, 1903, [*A*], 71, 405.

[2] Rutherford and Geiger, *ibid.*, 1908, [*A*], 81, 141, and Regener, *Verh. deut. physikal. Ges.*, 1908, 10, 78, 351.

[3] *Phil. Mag.*, 1914, [6], 552.

The velocity of the *a*-particle emitted from different substances varies, and the foregoing figure applies to that given off by the substance known as radium-C (p. 1525). On the other hand, the ratio *e*/*m* is constant. When the velocity of the *a*-particle falls below a certain limit, which is about 40 per cent. of the velocity given above, the particle ceases to produce the effects characteristic of radioactivity, and passes beyond the reach of our present experimental methods. When the velocity of an *a*-particle has thus been reduced, the particle seems to be brought to rest within a very short distance, so that it appears to be suddenly stopped after traversing a certain thickness of matter. The maximum distance which an *a*-particle can penetrate through air at normal temperature and pressure has been called by Bragg the *range* of the *a*-particle. The ionisation produced by an *a*-particle near the end of its range increases very rapidly and then suddenly vanishes. The range of different *a*-particles varies from 2·53 cm. to 8·17 cm.[1] and is characteristic of the particular product from which the *a*-particle is emitted.[2] A relation has been obtained by Geiger and Nuttall[3] between the range and the rate of decay of radioactive products. The nature of an *a*-particle has been the subject of much speculation, and many considerations point to its identity with an atom of helium. The value of *e*/*m* for a helium atom of atomic weight 4 carrying the same ionic charge as a hydrogen ion in electrolysis should be $2{\cdot}5 \times 10^3$, and we have seen that the value of *e*/*m* for an *a*-particle is almost exactly twice that number. Now Rutherford and Geiger[4] have shown that an *a*-particle is associated with twice the atomic charge, whence it follows that the atomic weight of the *a*-particle is 4, *i.e.*, that the *a*-particle is a charged atom of helium. This has been confirmed by direct experiment by Rutherford and Royds (p. 1520).

Associated with the expulsion of *a*-particles is the phenomenon of radioactive recoil. When an *a*-particle of mass *m* is emitted by an atom of mass *M* the residual atom, the mass of which must be *M*—*m*, will be projected in a direction opposite to that in which the *a*-particle is travelling with a velocity *V* given by the equation $(M-m)V = mv$, where v is the velocity of the α-particle. Now since the velocity of an α-particle is about 2×10^9 cm./sec., and since its atomic weight is 4 and that of a radioactive atom about 200, it follows, from the above equation, that the velocity with which the residual atom recoils must be 4×10^7 cm. per second. This atom which constitutes the next product (p. 1511) in the disintegration series to the product from which the α-particle is emitted, will travel a considerable distance if free to move through a vacuum, as has been shown by Russ and Makower.[1] The recoiling atom is positively charged and can be deflected in electric and magnetic fields, and this property can be used, as in the case of α-rays, to determine the velocity of projection and the value of $\frac{e}{m}$ for the recoiling atoms. The employment of this method affords a means of determining the atomic weights of several radioactive substances. When projected into air at atmospheric pressure, a recoil stream does not penetrate more than about a tenth of a millimetre; but the recoiling atoms after being stopped still retain their positive charges and can thus be collected on the negative electrode in an electric field. By this process many radioactive products have been separated.[2] Although an atom when it recoils possesses only $\frac{1}{50}$ the energy of the α-particle, it is able to produce ionisation in gases, as has been shown by Wertenstein.[3]

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[1] Geiger, *Zeit. f. Physik*, 1921, 8, 1, 45.

[2] It has recently been established by Rutherford and A. B. Wood (*Phil. Mag.*, 1921, [6], 41, 570 and 573) that in the disintegration of thorium active deposit a small number of *a*-particles (about one in ten thousand) is emitted with a range of 11·3 cm.

[3] *Phil. Mag.*, 1911, 22, 613.

[4] *Proc. Roy. Soc.*, 1908, [*A*], 81, 162.

654 If, as we have seen, the heavy radioactive atom recoils from the particle when it is expelled, it might be expected that an α-particle in its path through a substance of low atomic weight such as hydrogen would, under suitable conditions of impact, cause the light hydrogen atoms to recoil with considerable velocity. This was first observed to be the case by Marsden.[4] He observed that when α-particles passed through hydrogen, feeble scintillations could be detected at distances far beyond the range of the α-particle. The range of the recoil stream of hydrogen was found to be about four times that of the α-particles producing it, a value which agrees well with that calculated by Darwin[5] on Bohr's[6] theory of the absorption of α-particles by matter. Rutherford[7] has confirmed and extended these observations, and has

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[1] *Proc. Roy. Soc.*, 1909, [*A*], **82**, 205.

[2] Hahn, *Verh. deut. physikal. Ges.*, 1909, **11**, 55.

[3] *Le Radium*, 1912, **9**, 6.

[4] Marsden, *Phil. Mag.*, 1914, [6], **27**, 824.

[5] Darwin, *ibid.*, 499.

[6] Bohr, *ibid.*, 1913, [6], **25**, 10.

[7] Rutherford, *ibid.*, 1919, [6], **37**, 527, 563, 571, 581.

obtained results of far-reaching importance from the point of view of atomic structure. Whereas the results obtained with α-particles of short range (less than 4 cm. of air) are consistent with the simple theory of collisions between point atomic nuclei, the results for α-particles of long range such as those from radium-C (range 7 cm.) are entirely inconsistent with this view. In this case it can be calculated that when such collisions take place the nuclei of the two colliding atoms may come within a distance of about 3×10^{-13} cm., a distance which is less than the diameter of an electron. It was found that the number and distribution of the hydrogen atoms giving rise to scintillations are quite different from those to be expected if the nuclei were point charges repelling each other according to the inverse square law. The hydrogen atoms produced by such swift α-particles are shot forward mainly in the direction of the stream of α-particles producing them, and are nearly uniform in velocity. Rutherford explains these results by supposing that the helium nucleus behaves as a charged disc of radius 3×10^{-13} with its plane perpendicular to its direction of motion, and that in these very close collisions with hydrogen atoms such intense electric forces are involved that both the structure of the helium atom and possibly the electron itself may be deformed. In this way, the forces between the nuclei at very close distances might be greatly modified, although at greater distances the law of the inverse square would hold, as is known to be the case.

It can be calculated that, for all atoms carrying unit electric charge and of atomic weight less than 16, scintillations should appear beyond the range of the α-particles, and evidence has been obtained that this is the case with oxygen and nitrogen, but not with any heavier element.

The case of nitrogen is particularly remarkable, for besides the scintillations due to nitrogen atoms having a range slightly greater than the α-particles producing them, a few scintillations of much greater range are detectable. The evidence goes to show that these are caused by charged atoms of hydrogen produced by the disruption of the nitrogen nucleus, thus showing that the nitrogen nucleus contains hydrogen nuclei as a constituent. It seems probable that the nitrogen nucleus consists of three helium nuclei each of mass four and two hydrogen nuclei, giving to nitrogen the known atomic weight 14. This observation opens a new field of inquiry into the structure of atomic nuclei, for with α-particles of greater energy it should be possible to disintegrate other nuclei besides that of nitrogen. Analogous effects have, in fact, been observed with boron, fluorine, sodium, aluminium, and phosphorus.[1] It thus appears that some, if not all, of the elements are built up from helium and hydrogen nuclei. For the latter fundamental constituent of matter Rutherford has suggested the name *proton*.

655 When the β-particles are expelled from radium they carry with them negative electricity and must leave the radium positively charged. This is clearly shown by the contrivance called the *Radium clock*.[2] This consists of a small tube containing some radium compound, which is attached at its upper end by an insulating rod of quartz to the top of a wider tube within which it hangs. At the lower end of the small tube two thin gold leaves are attached, the outer surface of the tube having been coated with phosphoric acid to render it conducting. The larger tube is coated on the inside with tinfoil, connected to earth, and is exhausted as completely as possible to reduce the loss of charge consequent on ionisation of its gaseous contents. With 30 mgrms. of pure radium bromide the leaves are observed to diverge, until they touch a piece of metal connected to earth, when they collapse, and then gradually diverge again, this

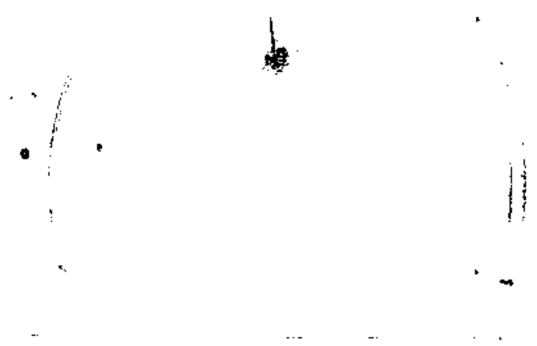

FIG. 212.—α-Rays from radium. Some of the α-particles have traversed the air before the expansion, others after the expansion.

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[1] Rutherford, *Proc. Phys. Soc. Lond.*, 1921, **33**, 389. See also Rutherford, "Artificial Disintegration of the Elements," *Journ. Chem. Soc.*, 1922, **121**, 400; and Rutherford and Chadwick, *Phil. Mag.*, 1921, **42**, 809.

[2] Strutt, *Phil. Mag.*, 1903, [6], **6**, 588.

periodic movement of the leaves occupying about a minute. The effect is due to the stoppage of the α-particles with their positive charge by the thin glass of the inner tube, which, however, allows the β-particles to pass through. The rhythmic motion continues with regularity for years, and it is estimated that it would take more than two thousand years for the emission of β-particles to fall to half its present rate, when the movement of the gold leaves would take place in two minutes instead of one.

The emission of β-rays from radioactive atoms is far more complicated than the emission of α-rays; for although, as in the case of α-rays, it seems possible that only one β-particle is emitted for each atom disintegrating,[1] the particles are emitted with very different velocities. By subjecting the radiation to a magnetic field the rays can be separated into definite groups known as a *magnetic spectrum*. It has been shown that in the case of radium and its disintegration products there are a great number of groups of rays.[2] It seems probable that the β-particles from any particular product are all projected with the same initial velocity, but that they are retarded to different extents while escaping from the atom.[3]

The phenomena involved in the passage of α-, β-, and γ-rays through air have been very strikingly demonstrated by C. T. R. Wilson.[4] When an α- or β-particle passes through air, very intense ionisation is produced in the track of the particle. If the air is saturated with water vapour, and if, by sudden expansion, the air is cooled immediately after the passage of the particle, a cloud is formed along its track. By a suitable timing device, an instantaneous photograph is obtained of the cloud, which thus renders visible the track of the particle. In the case of the α-particle the track is almost straight, showing only an occasional and sudden deflection or "scattering" from its course. At the

Fig. 213.—A complete α-ray from radium emanation.

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[1] Moseley, *Proc. Roy. Soc.*, 1912, [*A*], 87, 230.

[2] Danysz, *Le Radium*, 1913, 10, 5.

[3] Rutherford, *Phil. Mag.*, 1912, [6], 24, 453.

[4] *Proc. Roy. Soc.*, 1912, [*A*], 87, 277.

end of its range, the scattering of the α-particle is more marked (Fig. 212). The photographs exhibit also, on careful inspection, the ionisation produced by an atom recoiling from the α-particle when struck by it (Fig. 213). In the case of the β-particle, the path is much more tortuous, showing the greater part played by scattering in the case of these particles (Fig. 214). With γ-rays the photographs are much more complicated and consist of innumerable ramifications along the path of the rays. The photographs are such as to indicate that the ionisation is not

FIG. 214.—Ionisation by β-rays.

produced by the γ-rays themselves, but by secondary β-rays produced in their path—a suggestion first put forward by Bragg (Fig. 215).[1]

A remarkable property of the compounds of radium, first observed by Curie and Laborde,[2] is that of maintaining themselves constantly at a higher temperature than the surrounding atmosphere, the difference observed being from 3° to 5°. The continuous emission of heat which this shows was found by Curie and Dewar to be unaffected at the temperature of liquid air or liquid hydrogen. They found that 0·7 grm. of pure radium bromide, surrounded by liquid hydrogen, caused the volatilisation of 73 c.c. of hydrogen per minute. From data thus obtained it appears that one gram of radium emits nearly as much energy as would decompose one gram of water every day, or, otherwise expressed, that one pound of radium emits energy at the rate of about 11¼ horse-power.

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[1] *Phil. Mag.*, 1910, **20**, 365; *Proc. Roy. Soc.*, 1911, [*A*], **85**, 349.

[2] *Compt. rend.*, 1903, **136**, 673.

It does not seem possible that radium derives its enormous store of energy from external sources. The more probable supposition is that the α-particles are originally in rapid motion in the atom and that an α-particle when released from the atomic system flies off with the velocity it had in the atom.

The view that the energy emitted by radioactive bodies is derived from a store in the atoms is supported by the fact that the energy is given off at a rate which is quite unaffected by variations in physical and chemical conditions such as temperature, pressure, or mode of combination of the element; for it is difficult to account for these facts on any other supposition.

THE PRODUCTS OF RADIOACTIVE CHANGE.

656 A most remarkable property possessed by radium, actinium, and thorium, but not by uranium, is the power of giving off continuously a radioactive gas which can be condensed by extreme cold. The radioactivity of thorium was observed to vary capriciously, and this inconstancy was traced by Owens[1] to currents of air which removed the gas. Rutherford[2] gave the name of *emanation* to this remarkable gas, which discharges an electroscope, affects a photographic plate, diffuses through porous substances, and can be washed through water without loss of activity; it is condensed at the temperature of liquid air,[3]

FIG. 215.—Ionisation by γ-rays.

[1] *Phil. Mag.*, 1899, [5], 48, 360.

[2] *Ibid.*, 1900, [5], 49, 1.

[3] Rutherford and Soddy, *Phil. Mag.*, 1903, [6], 5, 561.

but not at that of solid carbon dioxide. It thus behaves differently from the ionised gas produced by X-rays, since the conductivity of such ionised gas is completely removed by passing through cotton wool, or by bubbling through water. The emanation from thorium rapidly loses its activity with time, falling to half value in about one minute.[1] Dorn[2] showed that radium compounds also gave off an active emanation, the amount obtained being much increased by heating the compound or by dissolving it in water.

These discoveries have led to the recognition of a hitherto unsuspected phenomenon, the spontaneous disintegration of the atoms of an element in a series of stages, each being marked by the emission of certain definite particles and in the case of α-ray transformations the production of a substance of lower atomic weight, characterised by definite physical and chemical properties. According to this *theory of the spontaneous disintegration of matter*, put forward by Rutherford and Soddy, in each second a proportion of the atoms of a radioactive material becomes unstable; these atoms break up with explosive violence, the change being accompanied by the expulsion of an α- or a β-particle. Thus the atom is to be regarded as a complex aggregate, which breaks up spontaneously with an evolution of energy enormous compared with that released in ordinary chemical action. These aggregates behave like atoms in that they cannot be split up by ordinary chemical or physical agencies.

The rate of change of any single product at any time is found to be proportional to the number of atoms present at that time, so that the change follows the same law as a monomolecular chemical reaction. Hence if N_0 represents the number of atoms of a radioactive substance present at any time, and N the number present after the lapse of time t, then:

$$N = N_0 e^{-\lambda t},$$

where λ is known as the *disintegration constant* of the substance, and e is the base of the natural logarithms. By differentiating this equation it is seen that:

$$\frac{dN}{dt} = -\lambda N.$$

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[1] Le Rossignol and Gimingham (*Phil. Mag.*, 1904, [6], 8, 107) found that the activity fell to half value in fifty-one seconds; Bronson (*Amer. J. Sci.*, 1905, 19, 185) found fifty-four seconds.

[2] *Naturforsch. Ges. Halle* (1900).

from which it follows that λ represents the fraction of the total number of atoms undergoing disintegration at any instant. The rate of disintegration of a substance is expressed by the constant λ; but it is more usual to define the rate of decay by the time T taken for half the number of atoms present to disintegrate. The value of T is connected with λ thus:

$$T = \frac{1}{\lambda}\log_e 2 = \frac{0{\cdot}693}{\lambda}.$$

The quantity T is known as the *period of half-change* of the substance, $\frac{1}{\lambda}$ being the *period of average life* of the atom.

When an active product is removed from a radioactive substance, *e.g.*, the emanation from a thorium compound, the activity of the isolated product gradually falls, according to the foregoing law, whilst that of the parent substance rises, also according to that law, owing to the accumulation of a fresh quantity of the active product. After the expiration of any period it is found that the isolated product has lost a certain fraction of its original activity whilst the parent substance has regained the same fraction of the activity which it had lost.

The determination of the exact series of changes undergone by a radioactive substance is a matter of considerable difficulty, and the solution of the problem is due largely to the brilliant researches of Rutherford and his colleagues. For this purpose it is necessary to measure separately the radioactivity due to the α-, the β-, and the γ-rays, and to construct curves showing the variation of each of these with time. The differentiation of the action of the three types of ray is effected by taking advantage of their different penetrating powers, sheets of metal of sufficient thickness to absorb the α-rays, or both the α- and β-rays, being interposed between the material and the electroscope. The β- and γ-rays are also often separated by deflecting the β-rays by a magnetic field.

From a comparison of the curves thus produced the number of changes which occur, the nature of the radiation, and the rate of the change can be deduced. The matter is much simplified when the products can be separated either physically or chemically from the parent substance and subjected to examination, as is the case with the emanation of radium, etc.

In most cases of radioactive changes, the products are formed from each other in a direct series of transformations. Thus any particular type of radioactive matter breaks up at a perfectly definite rate always giving rise to the same substance—the next member in the radioactive series. Some very interesting cases have, however, come to light in which it appears that certain types of atom can break up in two different ways, thus giving rise to two distinct products. This has been found to be the case with radium-C[1] (p. 1525), thorium-C,[2] and actinium-C (p. 1531–2). Thus radium-C usually disintegrates with the production of radium-D through the very short-lived product RaC′, but occasionally an atom of radium-C gives rise to another product, radium-C″, instead of radium-C′.[3] In the case of thorium-C the proportion of atoms giving rise to a branch product is much greater; for one-third of the atoms of thorium-C break up with the emission of α-rays and produce thorium-C″, whereas two-thirds emit β-rays and give rise to the product thorium-C′.[4] Both the C′ and C″ products seem to give rise to the D products (p. 1531). Another important case of a branch product is that of uranium-Y,[5] which forms the starting point of the actinium series (p. 1527).

Recently great interest has centred in the question of the position of the radioactive elements in Mendeléev's periodic system. It has been pointed out by Fajans[6] that when a transformation takes place with the emission of a β-particle the resulting product is more electronegative than the parent substance. Exactly the reverse is the case when a transformation takes place with the emission of an α-particle. It has been shown by Soddy[7] that during an α-ray transformation the atom passes from a family of even number in the periodic table to the next lower even family, the families of the odd numbers being always missed. This rule has been generalised and extended to include the case of β-ray transformations by Russell,[8] and by Fajans,[9] who has shown that in all cases in which the chemical nature of the radioactive products is sufficiently well known to test its correctness, the following rule holds: In an α-ray transformation the product generated falls into a group *two* places lower than that to which the parent substance belongs. On the other hand, in a β-ray transformation the product generated falls into a group *one* place higher than that of the parent substance. These laws are exemplified in the table (p. 1517). It will be seen that a single space in the periodic table is in each case occupied by several different products which are inseparable by any chemical process and can be distinguished only by their radioactive properties. Thus for instance Actinium-X, Thorium-X, Radium, and Mesothorium are inseparable by any chemical process. Here we have another example of *isotopic* elements (*cf.* pp. 74, 1498, 1517).

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[1] Hahn and Meitner, *Physikal. Zeit.*, 1909, **10**, 697.

[2] Hahn and Meitner, *Verh. deut. physikal. Ges.*, 1909, **11**, 55.

[3] Fajans, *Physikal. Zeit.*, 1911, **12**, 369.

[4] Marsden and Darwin, *Proc. Roy. Soc.*, 1912, [*A*], **87**, 17.

[5] Antonoff, *Phil. Mag.*, 1911, [6], **22**, 419.

[6] *Physikal. Zeit.*, 1913, **14**, 131.

[7] *Chemistry of the Radio-Elements*, p. 30.

[8] *Chem. News*, 1913, **107**, 49.

[9] *Ber.*, 1913, **46**, 422, and *Physikal. Zeit.*, 1913, **14**, 136.

RADIUM. Ra = 226. At. No. 88.

657 The mineral pitchblende—an impure oxide of uranium (p. 1149)—is the richest source of radioactive substances. Whilst investigating this material Mme. Curie found that some specimens of pitchblende had four times the activity of the metal uranium, and by chemical methods M. and Mme. Currie succeeded in separating two new substances, characterised by intense radioactivity, which they named polonium and radium.

The history of Mme. Curie's successful search for a radioactive substance in the residues of the pitchblende of Joachimsthal is of great interest.[1]

For the extraction of uranium the crushed ore is roasted with sodium carbonate, and washed with warm water and dilute sulphuric acid; the solution contains the uranium, and the insoluble residues are rejected. The Austrian Government presented Mme. Curie with a ton of these residues, the activity of which was found to be about four and a half times that of uranium. The residues consist chiefly of the sulphates of lead, barium, and calcium, silica, alumina, and oxide of iron, and contain also small amounts of copper, bismuth, zinc, cobalt, manganese, nickel, vanadium, antimony, thallium, the rare earths, columbium, tantalum, arsenic, etc. The search for the radioactive substances which cause the high activity of pitchblende was made in the early stages by the ordinary methods of chemical analysis. The residues were first treated with boiling soda, and the sodium sulphate formed removed by washing, together with lead, strontium, and aluminium. The insoluble portion was attacked by hydrochloric acid, which dissolves most of it. Th residue from this operation was found to contain a radioactiv substance which received the name *radium*. The solution als was found to contain radioactive substances, one of which is precipitated by sulphuretted hydrogen together with bismuth, and received the name *polonium*. A second, discovered by Debierne,[1] and named *actinium*, is contained in the hydroxide precipitated by ammonia in the filtrate from the precipitated sulphides.

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[1] See translation of thesis presented to the Faculté des Sciences of Paris, *Chem. News*, 1903, 88, 85.

658 *Purification and Properties of Radium Salts.*—The radium is extracted from the insoluble portion mentioned above by boiling with a strong solution of sodium carbonate, which transforms the barium and radium into carbonates. These are washed and dissolved in hydrochloric acid, and sulphuric acid is added, which precipitates the sulphates of barium and radium, with calcium, lead, iron, and a trace of actinium.

One ton of the Joachimsthal residues yielded from 10 to 20 kilos. of the crude sulphates, of an activity about 60 times that of uranium. The crude sulphate is next transformed into chloride, treated with sulphuretted hydrogen, the filtrate oxidised with chlorine, and precipitated with ammonia. The filtrate is then precipitated with sodium carbonate, and the carbonates are converted into chlorides, and washed with pure strong hydrochloric acid, which dissolves calcium sulphate, leaving barium and radium chlorides. These chlorides are then separated by repeated fractional crystallisation from water. When only a small quantity of crystals is allowed to separate, it is found that five times as much radium separates with the crystals as is left in solution. By repeating this process a great number of times a fraction of a gram of radium chloride was obtained of an activity a million times that of uranium.

Giesel[2] employs the bromides instead of chlorides in the fractional separation of radium and barium: the radium separates with the least soluble portion, and about eight fractionations effect the removal of most of the barium.

The compounds of radium resemble those of barium in properties. The crystals of the chloride are isomorphous with those of barium chloride; when pure they are colourless, but those containing both barium and radium become coloured yellow, orange, or pink. The solution in water evolves hydrogen and

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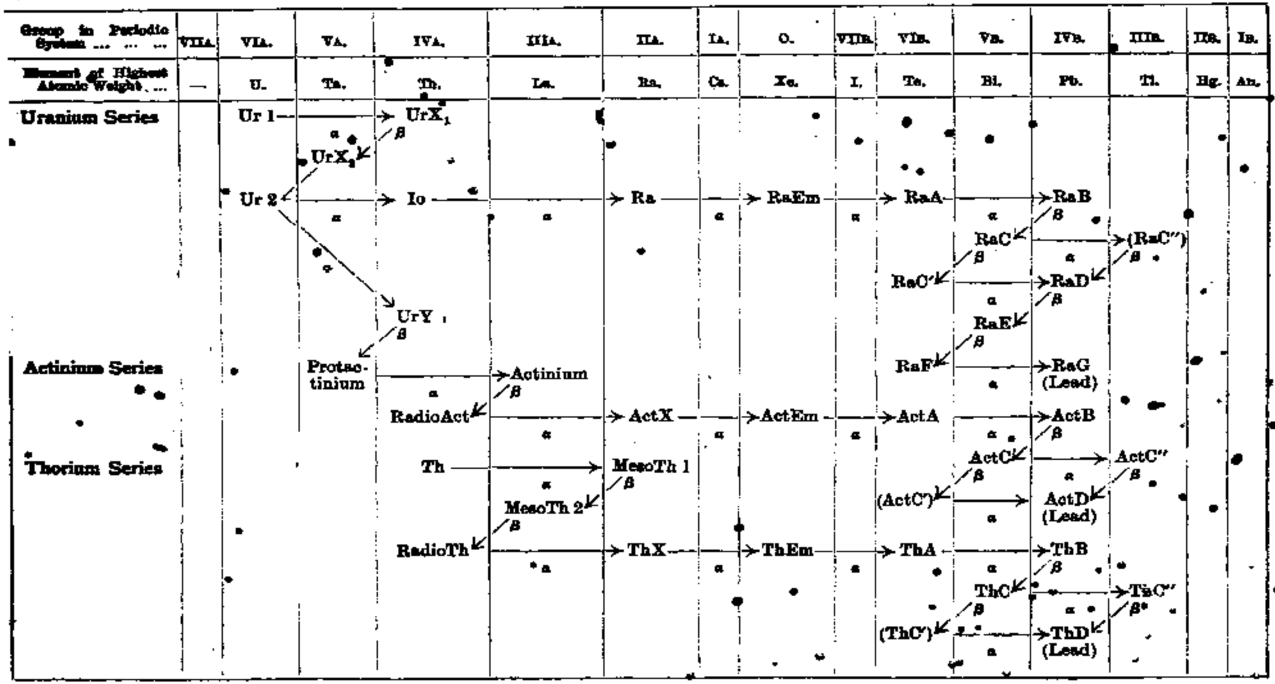
[1] *Compt. rend.*, 1899, 129, 593; 1900, 130, 906; 1903, 136, 446, 767.

[2] *Ann. Phys. Chem.*, 1899, [2], 69, 91; *Ber.*, 1902, 35, 3608.

A PERIODIC ARRANGEMENT OF THE RADIO-ELEMENTS.



oxygen continuously. The *nitrate, carbonate, sulphate, bromide* and *platinocyanide* resemble the corresponding salts of barium very closely. When freshly prepared the anhydrous bromide exhibits a splendid blue phosphorescence, which gradually disappears, but is more permanent in the presence of barium salts.

Radium has been prepared in the metallic state by Curie and Debierne.[1]

659 *Spectrum of Radium.*—Radium is found to have its own characteristic spectrum and this affords one of the strongest proofs of its elementary character. Radium bromide colours the Bunsen flame a pure carmine-red, and the flame shows four bands or lines in the red and a strong line in the blue.

The spectrum [2] of radium has been investigated by Demarçay,[3] Runge,[4] Exner, and Haschek,[5] Runge and Precht,[6] and Crookes.[7]

The most intense lines in the spark spectrum are 4633, 4436, 4341, 3814, 3650, 2814, and 2709.

660 *Atomic Weight of Radium.*—The atomic weight was determined by estimating the percentage of chlorine in the anhydrous chloride. As only about one decigram of substance was available, Mme. Curie [8] made preliminary determinations of the atomic weight of barium with about the same weight of pure barium chloride, and found that good results could be obtained. With barium chloride of an activity 600 times that of uranium the number 137 was obtained, with that of 7,500, the result was 143·8, and with chloride of increasing activity the atomic weight increased, giving about 225 with a specimen which only showed very faint traces of the brightest barium lines in the spectroscope. This sample was repurified, and gave the following results:

Radium chloride taken.	Silver chloride obtained.	Atomic weight (H = 1).
0·09192	0·08890	225·7
0·08936	0·08627	226·2
0·08839	0·08589	224·5

The activity of this chloride was about two million times that of uranium. A later determination made by Mme. Curie in 1907 gave the value 226·4,[1] and Thorpe[2] found the value 226·7. Ramsay and Gray[3] give the value 226·45. A determination with a large quantity of radium, which therefore probably gives the most trustworthy result, has been made by Hönigschmid,[4] who finds the atomic weight to be 225·95. This number is in harmony with the chemical behaviour of radium, which then finds its place in the periodic table in Group II, Series 12.

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[1] *Compt. rend.*, 1910, **151**, 523; *Le Radium*, 1910, **7**, 309.

[2] See Watts, *Index of Spectra* Appendix O, p. 40.

[3] *Compt. rend.*, 1898, **127**, 1218.

[4] *Ann. Physik*, 1903, **12**, 407.

[5] *Wien Ber.*, 1901, July 4.

[6] *Ann. Physik*, 1904, **14**, 418.

[7] *Proc. Roy. Soc.*, 1904, **72**, 295.

[8] *Compt. rend.*, 1899, **129**, 760; 1900, **131**, 382; 1902, **135**, 161.

Runge and Precht[5] have made calculations of the atomic weight of radium from the spectrum, and have deduced the value 256·3. This assumes that radium really belongs to the group of alkaline earths, and is based upon the observation that radium, like Mg, Ca, Sr, and Ba, has in its spectrum pairs of lines, repeated several times, with a constant difference of oscillation frequency, and that the distance apart of these pairs for the different elements increases in a regular manner with the atomic weight (p. 165).

It must be remembered that this calculation amounts to an *extra*polation passing over the unknown element below barium in the periodic table (Series 10), so that we are extrapolating for a considerable distance. It has been pointed out[6] that the result of the calculation is probably too high, for the reason that a similar calculation of the atomic weight of mercury from those of zinc and cadmium gives the atomic weight too high by about 22 units: it seems probable that this method has a tendency to give results too high for the higher atomic weights. A similar criticism has been made by Rudorf.[7] Furthermore, in the case of radium the atomic weight obtained by the spectroscopic method disagrees with strong evidence derived from a consideration of the disintegration theory (p. 1512); for there is reason to believe that radium is formed from uranium with the emission of three α-particles. Taking the atomic weight of uranium as 238 the atomic weight of radium should be 226, agreeing with the values found by chemical methods.

The question of establishing a standard quantity of radium was discussed at the International Congress of Radiology (Brussels, 1910). As a result 21·99 milligrams of the radium chloride used by Mme. Curie in the determination of the atomic weight of radium have been sealed in a small glass tube and deposited at Paris in the Bureau International des Poids et Mesures. A similar reserve standard has been deposited in Vienna. With the aid of these standards the quantity of radium in any sample can be estimated by comparing the γ-radiation it emits with that emitted by the standard.

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[1] *Compt. rend.*, 1907, **145**, 422.

[2] *Proc. Roy. Soc.*, 1908, [*A*], **80**, 298.

[3] *Proc. Roy. Soc.*, 1912, [*A*], **86**, 270.

[4] *Sitzungsber. K. Akad. Wiss. Wien*, 1911, IIa, **120**, 1617.

[5] *Phil. Mag.*, 1903, [6], **5**, 476. [6] Watts, *ibid.*, **6**, 64.

[7] *Zeit. physikal. Chem.*, 1904, **50**, 100.

PRODUCTS FORMED FROM RADIUM BY RADIOACTIVE CHANGE.

661 *Production of Helium by the Spontaneous Change of Radium.*—In 1903 Ramsay and Soddy[1] made the remarkable discovery that helium is given off by radium. They found that 30 milligrams of pure radium bromide (which had been prepared three months) when dissolved in water liberated gases amongst which were hydrogen and oxygen. These were removed by passing the gas over a red-hot spiral of partially oxidised copper wire, and then over phosphoric anhydride into a vacuum tube joined on to a small U-tube.

By placing the U-tube in liquid air most of the emanation present was condensed. The spectrum of the gas left in the vacuum tube, including the carbon dioxide present in the original gas, was then observed and showed the characteristic helium line D_3. In a repetition of the experiment the helium lines at 6677, 5876, 5016, 4922, 4713, and 4472 were observed as well as three unknown lines at 6180, 5695, and 5455. They also found that the emanation alone yielded helium in about three days.

These observations have been repeated and confirmed by Dewar and Curie[2] and by Himstedt and Meyer.[3] The latter observers sealed up 30 milligrams of radium bromide in an exhausted vacuum tube. The tube showed the lines of hydrogen and an oxide of carbon at first, but after four months the helium lines appeared.

Before the discovery of the production of helium in radioactive processes it was suggested by Rutherford and Soddy[4] that this gas might be a disintegration product of the radio-elements. This has since been proved by Rutherford and Royds[5] by sealing up some radium emanation in a glass tube, the thickness of the walls of which was only 0·01 millimetre. The α-particles which passed through the walls of this tube were collected in a vessel which surrounded it; after some days the spectrum of helium could be detected in the outer vessel, proving that the α-rays consisted of charged atoms of helium.

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[1] *Proc. Roy. Soc.*, 1903, 72, 204; 1904, 73, 346.

[2] *Compt. rend.*, 1904, 138, 190.

[3] *Ann. Physik*, 1904, 15, 184.

[4] *Phil. Mag.*, 1902, 4, 569; 1903, 5, 576.

[5] *Ibid.*, 1909, 17, 281.

The rate of production of helium from radium has been measured by Dewar,[1] and by Boltwood and Rutherford.[2] From one gram of radium (metallic) in equilibrium with the emanation, radium-A, and radium-C, the latter find that 156 cubic millimetres of helium are produced per year. Dewar found the value 169 cubic millimetres per year, which must, however, be slightly corrected to be comparable with the number found by Boltwood and Rutherford on account of the difference in the values of the radium standards used in the two sets of experiments. When thus corrected the value found by Dewar becomes 164 cubic millimetres. The volume of helium to be expected from theoretical considerations is 158 cubic millimetres per gram of radium per year.

662 *Radium Emanation.*—The emanation is continuously produced from radium compounds and is itself strongly radioactive. A portion of it escapes, but the remainder is occluded in the compound, adding its radiation to that of the radium compound. To this is due the phenomenon, observed by Curie, that the activity and emission of heat of radium compounds vary with their age, the activity increasing for about a month after preparation, when it becomes steady. This state of radioactive equilibrium is reached when the rate of production of fresh emanation balances the rate of change of that already formed.

The emanation is formed from radium by the expulsion of an α-particle and itself passes into the next lower product by a similar change. The period of half-change for radium is about 2,000 years, and for the emanation 3·85 days. By measuring the emanation from 0·06 gram of radium bromide, Ramsay and Soddy conclude that the maximum amount of emanation obtainable from one gram of radium is one cubic millimetre. This quantity is known as one *curie.* Later determinations by Rutherford,[3] Debierne,[4] and Gray and Ramsay[5] give the value 0·6 cubic millimetre.

The emanation is most readily obtained by dissolving the radium compound in water and removing the gases produced.

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[1] *Proc. Roy. Soc.*, 1908, [*A*], 81, 280; 1910, 83, 404.

[2] *Phil. Mag.*, 1911, 22, 586.

[3] *Ibid.*, 1908, 16, 300.

[4] *Compt. rend.*, 1909, 148, 1264.

[5] *Journ. Chem. Soc.*, 1909, 95, 1073.

This is best done by causing the solution to boil under reduced pressure. If air be passed through a radium solution large quantities of a mixture of air with the emanation may be obtained, and this may be stored in a gas-holder, and the electrical and photographic action examined for days after its production. The emanation can also be removed by heating the salt. When mixed with a large volume of air it condenses at −154°; but it must be remembered that in these circumstances the partial pressure of the emanation is exceedingly minute. When purified and at atmospheric pressure the emanation boils at − 65°.[1] When at very low partial pressures, the condensation point of the emanation seems to depend upon the nature of the surface upon which it condenses.[2] If the emanation obtained from a few milligrams of radium bromide by heating a solution be condensed in a small U-tube surrounded by liquid air, the U-tube being connected with a larger tube containing a small phosphorescent screen of zinc sulphide, and the whole apparatus connected with an air pump, the behaviour of the emanation can be watched by means of the phosphorescence of the screen. The apparatus being partially exhausted, and the U-tube immersed in liquid air, no luminosity of the screen is observed, but if the liquid air be removed, in a few minutes the emanation diffuses into the wider tube, and the screen becomes brightly phosphorescent. If the U-tube be re-immersed in liquid air the emanation re-condenses, but the phosphorescence of the screen dies away only slowly, being maintained for some time by the production of an active deposit on the glass.

In another experiment a quantity of the emanation was collected in a small glass tube, which was seen to phosphoresce brightly under the rays from the emanation, and in a dark room the passage of the emanation from point to point of the tube could be traced. On opening the tap which connected the tube with the pump the slow flow of the emanation through the capillary portion of the tube and its more rapid passage through the wider portions was well seen.

The emanation obeys Boyle's law. Attempts to determine its density by measuring its rate of diffusion show that it is a heavy gas, of a density about ·100; the method of diffusion is, however, for a variety of reasons unsuitable for determining the atomic weight of the emanation. From a consideration of the disintegration theory of radioactive changes, the atomic weight of radium emanation should be 222. Assuming the emanation to be monatomic, Gray and Ramsay[1] find the value 223, by a direct determination of its density with a specially constructed sensitive balance. The emanation belongs to the helium-argon group of gases, and like them resists attack by all chemical agents that have been tried. It is not affected when led in tubes over platinum black, copper oxide, zinc dust, etc., at a high temperature, and is unaffected by prolonged sparking with oxygen over caustic potash.

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[1] Rutherford, *Phil. Mag.*, 1909, 17, 723.

[2] Laborde, *Le Radium*, 1909, 6, 289; 1910, 7, 294; Boyle, *Phil. Mag.*, 1910, 20, 955.

The spectrum of the emanation was first examined by Ramsay and Collie,[2] and later by Rutherford and Royds,[3] Cameron and Ramsay,[4] Watson,[5] and Royds.[6] The brightest lines are those of wave-lengths: 4681·1, 4644·7, 4460·0, 4350·3, 4308·3, 4203·7, 4166·6, 4018·0, 3982·0, 3753·6, 3664·6.

Rutherford and Barnes[7] have made experiments on the heat emission by radium bromide and by the emanation obtained from it. The heat emission per gram of radium bromide was found to be 65 gram-calories per hour (which corresponds to 110 gram-calories per hour per gram of radium itself). The emanation was then driven off, and condensed by means of liquid air. After removal of the emanation the heat emission of the radium bromide fell off in three hours to about one-quarter (27%), and then slowly increased, reaching its original rate in about a month. The heat emission from the separated emanation rose to a maximum in three hours, and then slowly decayed, falling to a half value in about 3·7 days. The rate of decay of the emanation and the rate of recovery of the radium compound are both expressed by the exponential formula:

$$Q_t = Q\epsilon^{-\lambda t},$$

where Q is the heat emission at first, and Q_t that after a time t, λ being the constant of change. The radioactivity itself also follows a similar law, but the variation in the heat emission both of radium and of the emanation correspond approximately to the activity as measured by the α-rays and not to that of the β- or γ-rays. The heat emission of radium thus corresponds approximately with the expulsion of α-particles.

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[1] *Proc. Roy. Soc.*, 1911, [*A*], 84, 536.

[2] *Ibid.*, 1904, 73, 470.

[3] *Phil. Mag.*, 1908, 16, 313.

[4] *Proc. Roy. Soc.*, 1908, [*A*], 81, 210.

[5] *Ibid.*, [*A*], 1909, 83, 50.

[6] *Phil. Mag.*, 1909, 17, 202.

[7] *Ibid.*, 1904, [6], 7, 202.

The most recent and accurate determinations of the heating effect of radium are by Meyer and Hess,[1] and by Rutherford and Robinson.[2] The former give, for the heat emitted by one gram of radium in equilibrium with its disintegration products, the value 132·3 and the latter the value 135 gram-calories per hour. Rutherford and Robinson have also determined the heat emitted by each of the disintegration products separately, and also estimate that the β-rays contribute 3·5 per cent. and the γ-rays 4·8 per cent. of the total heating effect of radium. The observed heat emission is in good agreement with the calculated kinetic energy of the radiations. The heat emitted by radium and its products of disintegration is shown in the following table:

	Heating effect in gram-calories per hour, corresponding to one gram of radium.			
	α-Rays.	β-Rays.	γ-Rays.	Total.
Radium	25·1	—	—	25·1
Emanation	28·6	—	—	28·6
Radium-A	30·5	—	—	30·5
Radium-B } Radium-C }	39·4	4·7	6·4	50·5
Totals	123·6	4·7	6·4	134·7

When the emanation is left in contact with water, the latter is decomposed, a mixture of hydrogen and oxygen containing an excess of hydrogen being evolved. About 0·03 c.mm. of emanation yielded 2—4 c.c. of gas in different experiments, containing 3—14 per cent. of hydrogen in excess. The origin of this excess is not at present understood,[3] but it is probably in some way connected with the formation of ozone. The emanation is also capable of bringing about the slow combination of gaseous hydrogen and oxygen.

As already mentioned, the emanation on preservation yields helium, the volume of the latter being about three times as great as that of the emanation.[4]

663 *Radium-A*, *-B*, *-C*, *-D*, and *-E*.—The radium emanation induces radioactivity on the glass in which it is contained; on

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[1] *Wien Ber.*, 1912, **121**, 603.

[2] *Phil. Mag.*, 1913, **25**, 312.

[3] See Ramsay, *Journ. Chem. Soc.*, 1907, **91**, 931.

[4] Cameron and Ramsay, *Journ. Chem. Soc.*, 1907, **91**, 1266.

removing the emanation the excited activity at once commences to decay. This excited activity is due to the deposit on the surface of bodies of active matter, which can be removed by solution in acid, and recovered on evaporation of the solvent. It has the property of concentrating itself on a negatively charged wire. Such a wire placed in the presence of the radium emanation becomes strongly active, and if drawn across a screen of zinc sulphide, some of the active matter is rubbed off, leaving a luminous trail.

It has been ascertained that the deposited active matter from the radium emanation breaks up rapidly in successive and well-marked stages, yielding three ephemeral substances which have been named radium-A, radium-B, and radium-C; the first of these emits α-rays only, the last emits rays of all three kinds, and radium-B emits β- and γ-rays. The emanation is half transformed in 3·85 days: radium-A is half transformed in three minutes, radium-B takes 26·7 minutes, and radium-C 19·5 minutes for half transformation into a comparatively permanent product, radium-D. This requires 16·5 years for half transformation into radium-E, half of which is transformed in 5 days into radium-F. The complex nature of radium-C has already been discussed (p. 1514).

664. *Radium-F, Polonium, Radio-tellurium.*—During the investigation of the pitchblende residues from which radium was isolated, Mme. Curie obtained a second radioactive element to which the name of polonium was given. This substance was found by Mme. Curie to separate out with bismuth. She employed three methods of separation:

(*a*) Sublimation of the sulphides *in vacuo*: the active sulphide is the more volatile.

(*b*) Precipitation of the nitrate by water: the precipitate is the more active.

(*c*) Precipitation of a strongly acid solution of the chlorides by sulphuretted hydrogen: the precipitate is the more active.

Marckwald[1] obtained a radioactive substance with tellurium as an impurity, which he called radio-tellurium. It is undoubtedly the same as polonium. Marckwald found that if a plate of bismuth be immersed in a solution containing polonium the active matter is deposited on the plate, and the solution

[1] *Ber.*, 1902, 35, 2285, 4239; 1903, 36, 2662.

remains inactive. The active matter is also precipitated by treating the solution with stannous chloride. From fifteen tons of pitchblende Marckwald obtained sixteen grams of mixed selenium, tellurium, and polonium, from which, by treatment of the oxides with ammonia, an insoluble residue weighing three milligrams and containing all the active matter was obtained.

The radiation is extremely active, consisting entirely of α-rays. One-hundredth of a milligram produces intense phosphorescence in a screen of zinc sulphide. The period of half change is 136 days, and in this respect and in the nature of its radiation polonium agrees exactly with radium-F, with which it is doubtless to be identified.

Marckwald[1] considered that radio-tellurium or polonium would prove to be the missing element of the sulphur-selenium-tellurium family, a supposition which has since been confirmed. Since polonium (RaF), is produced from radium by changes involving the expulsion of four α-particles, it follows that the atomic weight of polonium should be $226 - 4 \times 4 = 210$. The product radium-G formed from polonium has therefore an atomic weight 206, and has been identified as an isotopic form of lead. Another isotope of lead has been separated from thorium minerals (p. 940).

The lead salts separated from pitchblende are also radioactive, but it has been shown that they owe their activity to the presence of the transformation products of radium known as radium-D, -E, and -F.

An interesting method of separating polonium from lead and radium-D by dialysis has been devised by Paneth,[2] who finds that polonium in solution behaves like a colloid and cannot diffuse through a membrane made of bladder or parchment. Making use of this property it is possible to separate polonium from lead salts and other impurities.

The properties of the various transformation products of radium are summarised in tabular form on p. 1531.

ACTINIUM. Ac = 226. At. No. 89.

665 Actinium, discovered by Debierne,[3] is, no doubt, the same substance as that described by Giesel[4] under the name of

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[1] *Ber.*, 1905, 38, 591.

[2] *Monatsh.*, 1913, 34, 401.

[3] *Compt. rend.*, 1899, 129, 593; 1900, 130, 206; 1903, 136, 446, 767.

[4] *Ber.*, 1902, 35, 3608; 1903, 36, 342; 1904, 37, 1696, 3963.

emanium. It was discovered in the precipitate of rare earths separated from pitchblende, the bulk of which consisted of thoria, and was finally obtained mixed with lanthana. It giv a characteristic emanation, and imparts activity to neighbouri objects.

Debierne has shown that actinium, like radium, gives ri to helium proportionate in quantity to the activity of t preparation.

The present state of knowledge regarding actinium summarised in the table on p. 1531.

Boltwood[1] has shown that the amount of actinium present uranium minerals is approximately proportional to the urani content of the mineral. This fact suggests a genetic connecti between actinium and uranium, but actinium is not in the dire series of disintegration products of uranium. The connecti between uranium and actinium has been established by Hahn and Meitner,[2] who showed that actinium is derived from uranium 2 through the branch product uranium-Y (p. 1532), and a new product of very long life which they called *protactinium*.

THORIUM. Th = 232·4. At. No. 90.

666 As already mentioned, the radioactivity of thorium was discovered by Schmidt and by Mme. Curie, and the existence of an emanation by Rutherford.

Rutherford and Soddy,[3] by adding ammonia to a solution of a thorium salt, so as to precipitate the thorium as hydroxide, found that the filtrate contained a substance many times more active than the thorium itself. This active constituent they named thorium-X: in a month's time it had completely lost its activity while the thorium had completely recovered its original activity. The decay of activity of the thorium-X, and the recovery of the activity of the thorium, are found to be represented by exactly similar curves; the time required for decay to half value, or for the recovery of half the lost activity, being in each case 3·7 days.

Thorium-X appears not to be formed directly from thorium, but through three intermediate products, mesothorium 1, mesothorium 2, and radiothorium.[1] Radiothorium cannot b separated from thorium by any known chemical process, no can mesothorium 1 be separated from thorium-X; but the firs two substances can be separated from the second two by addin excess of ammonia to a solution of thorium nitrate. Th further changes undergone by this substance are summarised on p. 1521.

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[1] *Amer. J. Sci.*, 1908, 25, 269.

[2] Hahn and Meitner, *Phys. Zeit.*, 1918, 19, 208; 1919, 20, 127, 529; also Hahn, *Phys. Zeit.*, 1920, 21, 591.

[3] *Phil. Mag.*, 1906, [6], 4, 370, 569.

The final product of disintegration of thorium has been shown to be an isotopic form of lead, the atomic weight of which should from theoretical considerations be 208. Estimations of the atomic weight of lead separated from Ceylon-thorite give the values 207·74 [2] and 207·77,[3] the difference between these numbers and the theoretical number (208) being no doubt due to a slight admixture of lead derived from radium with atomic weight 206. This demonstration of the existence of two forms of lead with atomic weights 206 and 208 respectively affords one of the most direct and striking proofs of the theory of isotopes.

Thorium, radium, and actinium exhibit many points of similarity; each gives an emanation whose life is short; these emanations have no definite combining properties, and belong to the helium-argon group of inert gases; in each case the emanation gives rise to a non-volatile substance (thorium-A, radium-A, actinium-A) which deposits on the surface of bodies, and is concentrated on the negative electrode in an electric field. The emanations and the subsequent disintegration products show very striking analogies both with regard to the radiations emitted by each product and other properties. This can be seen from the table given on p. 1531.

URANIUM. U = 238·2. At. No. 92.

667 The discovery of the radioactivity of uranium by H. Becquerel, in 1896 was, as already mentioned (p. 1490), the starting point of the series of brilliant investigations by which the science of radioactivity has been established. There is strong evidence derived from the radioactive properties of uranium that this body really consists of two distinct elements which, however, are so similar to each other as to be inseparable

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[1] Hahn, *Proc. Roy. Soc.* 1906, [*A*], 76, 115; *Ber.*, 1907, 40, 1462; *Physikal. Zeit.*, 1907, 8, 277; *ibid.*, 1908, 9, 246.

[2] Soddy, *Science Abs.*, 1915, 602.

[3] Hönigschmid, *Zeit. Elektrochem.*, 1917, 23, 161; *Phys. Zeit.*, 1917, 18, 114.

by chemical methods. The evidence rests on the fact, first noticed by Boltwood and subsequently confirmed by Geiger and Rutherford,[1] that an atom of uranium appears to give out two α-particles during the disintegration instead of one, as is the case with most radioactive atoms emitting α-rays. This fact can only be explained either by supposing uranium to consist of two successive disintegration products, or by assuming that an atom of uranium gives out two α-particles simultaneously. The latter hypothesis has been disproved by Marsden and Barratt,[2] and Geiger and Nuttall[3] have shown that the α-particles are not homogeneous. The two types of uranium are known as uranium 1 and uranium 2, the half change period of one of which is 5×10^9 years.

Von Hevesy[4] has shown that the valencies of the radio-elements can be found by observations on their rates of diffusion and mobilities in solution. It is shown that at any rate in many cases the expulsion of an α-particle by a parent substance gives rise to a change of valency of two units in the resulting product. It has been shown by von Hevesy and von Putnoky[5] that uranium 1 and uranium 2 cannot be separated by diffusion and that uranium 2 is not only very similar to uranium 1, but has also the same valency as that element. In fact they are isotopes.

Crookes showed[6] that by a single chemical operation, viz. by precipitating a uranium salt with ammonium carbonate in excess, the whole of the photographic activity of uranium was concentrated in the precipitate, and the uranium lef in solution was photographically inactive. The precipitate containing a substance which he called Uranium-X was, photographically, many hundred times as active as the uranium from which it had been separated. Becquerel[7] found that on adding barium chloride to a solution of uranium salt and precipitating as barium sulphate, the precipitate was strongly active, photographically, and the uranium had lost its activity. A year later it was found that the barium had become inactive, whilst the uranium had completely regained its activity.

The uranium deprived of uranium-X, although photographically inactive, is electrically active, this being due to the fact that the α-particle which it emits is incapable of producing much photographic action. Uranium-X can also be separated from uranium salts by boiling with lampblack, which retains this product.[1] Uranium-X emits only β- and γ-rays and has been shown to consist of two products, uranium-X_1 and uranium-X_2, having half change periods of 24·6 days and 1·17 minutes respectively.[2] They are intermediate between uranium 1 and uranium 2, which passes into *ionium*, the parent of radium.

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[1] *Phil. Mag.*, 1910, **20**, 691.

[2] *Proc. Phys. Soc.*, 1911, **23**, 367.

[3] *Phil. Mag.*, 1912, **23**, 439.

[4] *Ibid.*, 1913, **25**, 390.

[5] *Ibid.*, **25**, 415.

[6] *Proc. Roy. Soc.*, 1900, **66**, 409.

[7] *Compt. rend.*, 1900, **131**, 137; 1901, **133**, 977.

668 *Relation of Uranium and Radium.*—The further history of the transformation of uranium is interesting, for many facts point to the conclusion that radium is one of its transformation products. This was first surmised from the fact that the radioactivity of the uranium minerals is proportional to the quantity of uranium present[3] (in the absence of thorium). The ratio of uranium to radium in such minerals is almost constant,[4] and these facts are most readily explained by the supposition that the radium is actually formed from the uranium. The production of radium from uranium has been measured by Soddy,[5] and by Boltwood,[6] who carefully freed uranium from radium and measured by the emanation test the amount of radium present after the lapse of a year or two. It was found that the rate of production of radium was far less than was to be expected if radium were formed directly from uranium. This seemed to indicate the existence of an intermediate product of slow rate of decay. This product has since been separated from carnotite by Boltwood,[7] who gave it the name *ionium*. This element is the direct predecessor of radium in the disintegration series. From measurements on the rate of growth of radium from uranium Soddy[8] suggested that the half-change period of ionium is of the order 100,000 years. This value is confirmed by Geiger and Nuttall, who, having determined the range of the α-particle from ionium, deduced its half-change period to be 200,000 years (p. 1505).

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[1] Becquerel, *Compt. rend.*, 1905, 141, 485.

[2] Fajans and Göhring, *Die Naturwissenschaften*, 1913, 1, 339.

[3] McCoy, *Ber.*, 1904, 37, 2641.

[4] Strutt, *Proc. Roy. Soc.*, 1905, 76 [*A*], 88, 312; Boltwood, *Phil. Mag.*, 1905, [6], 9, 599.

[5] *Phil. Mag.*, 1905, [6], 9, 768; 1908, 16, 632; 1909, 18, 846; 1910, 20, 340.

[6] *Amer. J. Sci.*, 1905, 20, 239.

[7] *Ibid.*, 1906, 22, 537; 1907, 24, 370; 1908, 25, 365.

[8] *Phil. Mag.*, 1909, 18, 858.

669 The following tables summarise our present knowledge of the active products of disintegration of the radio-elements. The column headed *half-change period* gives the time of falling to half activity, or the time required for half the substance to be transformed into the next product.

URANIUM-RADIUM SERIES.

Product.	Half-change Period.	Rays emitted and Ranges of α-particles in cm. at 0°.	Atomic Weight.	Group in Periodic Table to which Product belongs.
Uranium 1	5×10^9 years	α (2·53)	238	VI*A*
Uranium-X_1	24·6 days	β, γ	234	IV*A*
Uranium-X_2	1·17 minutes	β, γ	234	V*A*
Uranium 2	2×10^6 years	α (2·91)	234	VI*A*
(Uranium-*Y*)	25·5 hours	β	230	IV*A*
Ionium	2×10^5 years	α (3·03)	230	IV*A*
Radium	2000 years	α, β (3·21)	226	II*A*
Radium emanation	3·85 days	α (3·91)	222	0
Radium-*A*	3·0 minutes	α (4·48)	218	VI*B*
Radium-*B*	26·7 minutes	β, γ	214	IV*B*
Radium-*C*	19·5 minutes	β, γ	214	V*B*
Radium-*C′*	10^{-6} seconds	α (6·61)	214	VI*B*
(Radium-*C″*)	1·4 minutes	β	210	III*B*
Radium-*D*	16·5 years	β, γ	210	IV*B*
Radium-*E*	5 days	β, γ	210	V*B*
Radium-*F* (Polonium)	136 days	α (3·72)	210	VI*B*
Radium-*G* (Lead)	—	—	206	IV*B*

THORIUM SERIES.

Product.	Half-change Period.	Rays emitted and Ranges in cm. of α-particles in air at 0°.	Atomic Weight.	Group in Periodic Table to which Product belongs.
Thorium	$1 \cdot 3 \times 10^{10}$ years	α (2·75)	232	IV*A*
Mesothorium 1	6·7 years	—	228	II*A*
Mesothorium 2	6·2 hours	β, γ	228	III*A*
Radio-thorium	1·9 years	α (3·81)	228	IV*A*
Thorium-*X*	3·7 days	α, β (4·13)	224	II*A*
Thorium emanation	54·5 seconds	α (4·80)	220	0
Thorium-*A*	0·14 second	α (5·39)	216	VI*B*
Thorium-*B*	10·6 hours	β, γ	212	IV*B*
Thorium-*C*	60·8 minutes	α, β (4·54)	212	V*B*
(Thorium-*C′*)	(?) 10^{-11} sec.	α (8·17)	212	VI*B*
Thorium-*C″*	3·1 minutes	β, γ	208	III*B*
Thorium-*D* (Lead)	—	—	208	IV*B*

ACTINIUM SERIES.

Product.	Half-change Period.	Rays emitted, and Ranges of α-particles in cm. at 0°.	Atomic Weight.	Group in Periodic Table to which Product belongs.
Protactinium	12,000 years .	α (3·48)	230	V*A*
Actinium	20 years . .	—	226	III*A*
Radio-actinium . .	19·5 days . .	α (4·43)	226	IV*A*
Actinium-*X*	11·6 days . .	α (4·14)	222	II*A*
Actinium emanation .	3·9 seconds .	α (5·49)	218	0
Actinium-*A*	0·002 second .	α (6·24)	214	VI*B*
Actinium-*B*	36·3 minutes .	β, γ	210	IV*B*
Actinium-*C*	2·15 minutes .	α, β (5·22)	210	V*B*
(Actinium-*C′*)	very short .	α (6·10)	210	VI*B*
Actinium-*C″*	4·71 minutes .	β, γ	206	III*B*

Products in brackets are branch products.

670. The discovery that the atoms of certain heavy elements undergo continuous spontaneous disintegration with the formation of new substances necessitates a profound modification of our conceptions of chemical atoms. Much information regarding atomic structures has been obtained of recent years on this subject from other sources, and it becomes important to coordinate the knowledge thus obtained with radioactive phenomena.

From a consideration of the absorption of cathode rays of high velocity, Lenard[1] expressed the view that these rays would penetrate atoms and that only a very small part of the atom was impervious to them. The same conclusion has been reached and elaborated by Rutherford as a result of his investigations of the two kinds of scattering of α-particles on passing through thin metal foil. The first type, a small angle scattering proceeding according to the ordinary laws of probability, need not be considered here, but the second type, consisting of a very occasional scattering through large angles, is of fundamental importance. The nature and distribution of this scattering have been studied in great detail by Geiger and Marsden,[2] and an explanation of their results has been given by Rutherford[3] on the supposition that the atom is the seat of intense electric forces whereby the α-particle can under suitable conditions be deflected through angles greater than a right angle by a single encounter with an atom. To produce these intense fields, the atom is supposed to consist of a small positively charged "nucleus" surrounded by a number of rotating electrons which neutralise the charge on the nucleus. In its passage through the atom, the α-particle is attracted by the electrons producing small angle scattering and repelled by the nucleus, and it is by passing sufficiently closely to the nucleus that the large angle scattering mentioned above takes place. The dimensions of the nucleus have been estimated by Darwin to be of the order 10^{-13} cm.[1] Since the atom is electrically neutral, it follows that the charge on the nucleus is equal to the number of electrons in the atom, which in turn can be shown, from the results of scattering, to be approximately equal to half the atomic weight of the atom in question. Since half the atomic weight of an element is in most cases nearly equal to the "atomic number" or position of an element in the periodic table, the above considerations suggest that for any element the nuclear charge, and therefore the number of electrons in an atom, is equal to the atomic number of the element, an idea which, as we shall see later, is substantiated by other evidence. According to this view each element in the periodic table contains one electron more than the preceding element, and an atom must be regarded as analogous to a planetary system consisting of a positively charged nucleus surrounded by electrons, equal in number to the atomic number of the element and rotating round the nucleus to produce stability. The α-particle on entering the planetary system behaves like a comet, passing in general almost straight through the atom, but being deflected along a hyperbolic path if it happens to pass sufficiently near to the nucleus.

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[1] *Ann. Physik*, 1903, 12, 714.

[2] *Proc. Roy. Soc.*, 1909, [*A*], 82, 495.

[3] *Phil. Mag.*, 1911, 21, 669.

This conception of atomic structure has been elaborated by Bohr,[2] and later by Sommerfeld, from a consideration of spectroscopic evidence, particularly for the cases of hydrogen and helium, which are relatively simple. The hydrogen atom is the simplest possible, for which the atomic number is 1. It consists of a singly-charged positive nucleus, about which rotates a single electron. In general, the orbits of the electrons in any atom will be elliptical, but the general atomic properties may be described by considering them as circular. According to the ordinary principles of dynamics, the electron could be considered to be rotating in an orbit of any radius provided that it is given a velocity of rotation which will balance the attraction of th nucleus. Such a system would radiate energy, and it is to Boh that we owe the conception that there are certain non-radiatin orbits of specified radius representing special stable states o the system. Radiation is supposed to take place only whe the electron passes from one position of stability to another. The possible stable orbits are determined by certain relations demanded by Planck's quantum theory, and while the view is in conflict with the classical laws of dynamics, it is demanded both by the existence of distinct and sharp spectral lines and by the permanence of the atom. The hydrogen ion consists of the isolated nucleus the dimensions of which is minute compared with atomic magnitudes. The case of the helium atom is much more complicated, since it consists of a doubly-charged nucleus surrounded by two rotating electrons. It is not proposed to discuss here in detail the constitution of the helium or more complicated atoms, but this conception of the helium atom is of importance from our point of view, in that it gives definite information regarding the nature of the α-particle. By the loss of two electrons we arrive at a doubly-charged nucleus of sub-atomic dimensions—the α-particle. The properties of the α-particle discussed above then become clear—its power of penetrating matter, and its occasional large angle scattering on passing through an atom in the neighbourhood of the nucleus, the absence of any emission of light by α-particles (for there are no electrons to emit any), and its ultimate transformation into helium by attracting two electrons.

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[1] C. G. Darwin, *Phil. Mag.*, 1914, 27, 506.

[2] *Phil. Mag.*, 1913, 26, 476, 857; 1915, 29, 332; 1915, 30, 394.

The importance of the atomic number as compared with the atomic weight of an element has been substantiated by other evidence besides that derived from the scattering of α-particles mentioned above—notably from a study of *X*-ray spectra. Here, too, the idea of the atomic number brings order into phenomena where confusion reigns in terms of atomic weights.

When white light falls upon an ordinary diffraction grating the transmitted or reflected light is found to be broken up into well-defined spectra of different orders according to well-known laws. Laue was the first to recognise that a crystal afforded an example of a space grating in which the distances between the component atoms forming the crystal are so small that the crystal should behave towards rays of very short wave-length much as a diffraction grating behaves towards ordinary light. If, as seemed probable, *X*-rays consisted of ether vibrations having wave-lengths of the order 10^{-8} cm., the crystalline space grating would be of the right dimensions to produce *X*-ray spectra. Laue's idea has been brilliantly justified by the experiments of Laue, Friedrich, and Knipping,[1] in which it was shown that *X*-rays can be diffracted by passing through crystals, thus establishing beyond doubt that the *X*-rays consist of ether waves of extremely short wave-length. This phenomenon supplied at once the means of investigating the structure of crystals, and of measuring the wave-lengths of the *X*-radiations emitted from anticathodes of different materials when used in a discharge tube. The question of crystal structure is beyond the scope of this section (but see p. 213), but the investigation of *X*-ray spectra from different elements has contributed much to our knowledge of atomic structure, and the results obtained will be briefly reviewed.

The general theory of the space grating is not altogether simple, but fortunately the diffraction effects produced by crystals on *X*-rays can be treated in a simple manner by considering certain planes of symmetry in the crystal as equivalent to reflecting surfaces selectively reflecting special wave-lengths. It can be shown that if *X*-rays impinge on such a plane of a crystal at an angle θ, then maxima of intensity will occur if

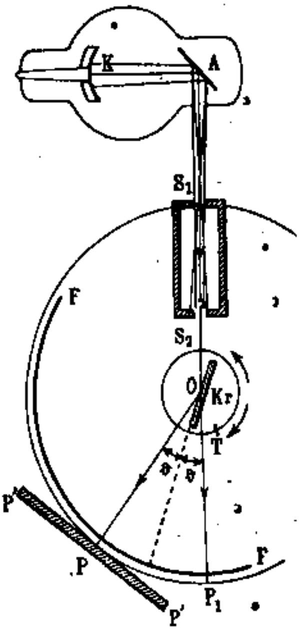

FIG. 216.

$$2d \sin \theta = n\lambda,$$

where *d* is the grating constant, λ the wave-length of the radiation, and *n* an integer.

In Fig. 216 is shown a typical piece of apparatus for obtaining spectra. The rays from the anticathode, A, after passing through suitably situated slits, S_1, S_2, placed to confine the beam fall upon a crystal at Θ and, if of wave-length such as to conform with the equation just given, are reflected on to a photographic plate or ionisation chamber placed at P. By rotating the crystal rays of different wave-lengths can be brought into action.

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[1] *Loc. cit.*

Prior to the discovery of the diffraction of *X*-rays by crystals Barkla[1] had shown that when cathode or *X*-rays impinge on different elements, certain characteristic secondary radiations are emitted by each element. The phenomenon was studied by observations on the penetrating power, or hardness, of the secondary rays emitted, and it was shown that the hardness of the secondary rays increases with the atomic weight of the element upon which the primary radiation falls. The characteristic radiation emitted by an element was thus seen to be an atomic property depending on its atomic weight. Barkla showed that the characteristic radiation fell into two series which he called *K*- and *L*-radiations (a third type, the *M*-radiation, has since been discovered by Siegbahn). On account of the fact that the characteristic rays were always softer than the exciting primary rays, Barkla described the secondary radiation as fluorescence radiations by analogy with fluorescence as observed in optics.

The detailed study of these phenomena and their explanation according to modern views on atomic structure has become possible by the application of the method of spectrum analysis. Moseley[2] was the first to make a systematic study of the elements by this method, and to bring out the importance of the atomic number of an element in this connection. The method of spectrum analysis and the introduction of the idea of atomic numbers as opposed to atomic weights renders the results at once definite and simple to interpret.

In Moseley's experiments cathode rays were allowed to fall on anticathodes of different metals which could be changed at will, and the *X*-radiation thus produced was examined by means of a crystal as described above. The *K*-radiation from elements ranging from Ca (atomic number, Z, $= 20$) to Cu (atomic number, Z, $= 29$) were examined and the results shown in Fig. 217 were obtained. From an examination of the figure it appears that the pair of lines emitted by each element and known as the K_{α}-and K_{β}-line respectively move regularly to positions of smaller wave-lengths with increasing atomic numbers and in such a way that the more intense and softer K_α-line can be represented in a manner similar to that given by Balmer for the hydrogen series in optics represented by the formula

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[1] *Phil. Mag.*, 1909, 17, 739; 1911, 21, 270.

[2] *Ibid.*, 1913, 26, 1024; 1914, 27, 703.

$$\nu = \tfrac{3}{4}N(Z-1)^2$$

where ν is the frequency of the vibration, Z the atomic number of the element, and N the well-known Balmer constant. The results obtained by Moseley for the K series have been extended by Siegbahn to the L series, and a newly-discovered M series.[1]

FIG. 217.

The general results obtained by him are shown in Fig. 218, in which the atomic numbers as ordinates are plotted against wavelengths as abscissæ. It is at once evident that the frequencies of the characteristic vibrations progress regularly with increase of atomic number as previously shown by Moseley.

These important results receive a simple explanation on the theory of atomic constitution propounded by Rutherford to account for the scattering of α-particles, and elaborated by Bohr from spectroscopic evidence. As we have seen, the atom is regarded as consisting of a positively charged nucleus surrounded by rings of electrons rotating in approximately circular orbits. From evidence deduced from the periodicity of atomi volumes and other phenomena, it may be supposed that as w proceed through the periodic system of elements adding one new electron as we pass from one element to the next of higher atomic number, a new ring of electrons is added successively as we reach each univalent alkali element. Proceeding from the nucleus outwards the successive rings are known as the *K*-, *L*-, *M*-, *N*-, etc., rings respectively. Without going into any detail as

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[1] Siegbahn, *Verh. d. Deutsch. Phys. Ges.*, 1916, 18, 278, and Stenström, *Ann. Physik*, 1918, 57, 347.

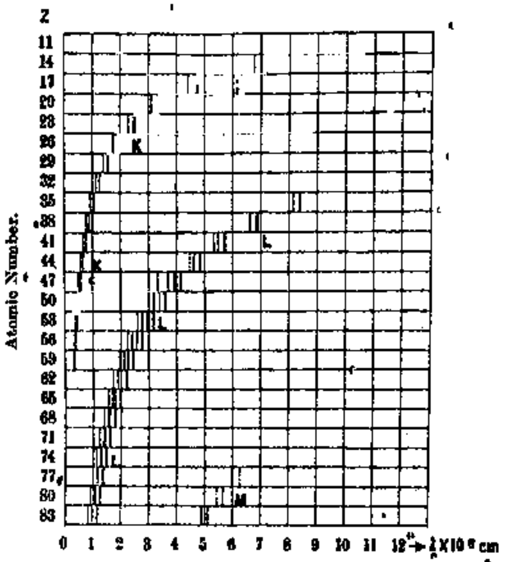

Fig. 218.

to the exact nature and orientation in space of these successive rings, it is supposed that, to produce *K*-radiation by cathode or *X*-rays, it is necessary to remove an electron from the innermost or *K*-ring, and similarly for the *L*- and *M*-radiations to remove an electron from one of these rings respectively. Suppose now, for example, that an electron has been removed by a primary radiation from the *K*-ring of any atom, the atom will then be in a position to emit characteristic *K*-radiation, and this may take place by electrons from the *L*-, *M*-, *N*-rings, etc., falling back into the *K*-ring with the production of radiation known as K_α-, K_β-, K_γ-radiation, etc. The same thing will happen with the *L* series, and radiation will be emitted by the atom by the transference of electrons to the L-ring from the outer M-, N-rings, etc. Thus we see in general that K-radiations are produced when an electron falls from an outer ring into the K-ring, and so on. The series of K-lines discovered by Moseley and shown in Fig. 218 are produced by electrons falling respectively from the L- and M-rings into the K-ring, and the reason that only two lines were observed in these experiments is to be found in the fact that the resolution employed was insufficient to detect lines due to electrons coming from the outer rings. With higher resolution the characteristic X-ray spectra can be shown to be more complicated, the K_α-line being broken up into a doublet.

We now obtain an explanation of Moseley's formula (p. 1537) on Bohr's theory, in which the energy of the L-ring is given by

$$W_a = Nh\frac{(Z-1)^2}{2^2}$$

where h is the fundamental constant in Planck's quantum theory. Similarly for the K-ring,

$$W_b = Nh\frac{(Z-1)^2}{1^2}$$

Then the energy emitted when the electron falls from the L-ring into the K-ring, giving rise to the K-radiation, is given by the relation

$$W_a - W_b = \nu h = Nh(Z-1)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

whence $$\nu = \tfrac{3}{4}N(Z-1)^2$$

It is not possible to consider here any of the finer points regarding X-ray and other spectra, and the reader is referred to special treatises on the subject.[1]

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[1] Cf. Sommerfeld, *Atombau und Spektrallinien* (Vieweg, 1919).

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